ATOMIC FORM

with

Special reference to the Configuration

of the

CARBON ATOM

BY

EDWARD E PRICE

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PREFACE

IT is more than 20 years ago that the author was first
led to the consideration of the Theory of Atomic
Form, and shortly afterwards commenced to make
models of tetrahedra of various forms with the view of
ascertaining how far such a figure would be capable
of fulfilling the rôle of the carbon atom   The author
concentrated his attention upon the form of an irregular
tetrahedron, particulars of which are given in the pages
of this book, and large numbers of models of this form
have been made, and combined in various ways in order
to represent the various types of carbon compounds

The work was suspended in 1914 by the exigencies
of the War, and the urgent demands of a professional
business, hence the delay in submitting the results to
public estimation

At the present time the constitution of the Atom is
the subject of physical theories which are widely separa-
ted from the ideas which have been set out in this book,
and many persons may be disposed to lay it aside as
being inconsistent with the latest advances of scientific
thought   The author asks for a more impartial con-
sideration of this subject , so much has yet to be dis-
covered, so many problems have yet to be elucidated,
that no Theory should be rejected which helps in any
way the consideration of these problems

It is also suggested that some persons who may not at present see their way to accept the theory of Atomic Form, may yet find the models of aggregates of the carbonoid an assistance when considering some of the problems of Organic Chemistry—by enabling them more easily to visualize the structures in three dimensions which undoubtedly are represented by chemical formulæ

The author desires to thank Mr I D Margary, M A, who has read the manuscript, for his kind assistance and many valuable suggestions

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CHAPTER I

INTRODUCTORY

IN any discussion of the constitution of the Atom the phenomenon of crystallization must have an important place, and it may be justly said that no theories of atomic or molecular constitution, which ignore the facts connected with the crystallization of the Elements, can be considered as resting on a sound basis

When an elementary substance is in a gaseous condition enclosed in a vacuum tube and subjected to forces relatively of great magnitude, there must necessarily be great difficulty in separating the phenomena produced by these conditions and by the rapid movements (both rotational and translatory) of the atom, from those characteristics that belong exclusively to the atom itself If these characteristics are studied when the atoms are in a state of approximate rest, they afford a much more satisfactory field for investigation, and more reliable results may be expected

The following statement of facts in connection with the crystallization of elementary substances is submitted

(1) A large proportion of the Elements are known to assume a crystalline structure when in the solid state, and of those which are not so known, many are capable of forming crystalline space-lattices when in combination with other Elements

   Some elementary substances which are liquid or gaseous at Ordinary Temperatures, may not have been examined in the solid state under conditions which produce the crystalline form

(2) Of those Elements which are known to crystallize each one forms its own particular crystal or space-lattice Some elements crystallize in more than one geometric form, but these cases do not invalidate the general rule stated above [1]

(3) Crystal formation is not affected or controlled in any way by physical forces other than heat, pressure and solubility Electricity plays no part in the formation of a crystal, and a magnetic field has no effect upon the process

(4) The space lattices vary as regards density ; i e , the atoms are more closely packed in some crystals than in others Sulphur forms crystals in two forms—Rhombic and Monoclinic, the latter readily changing into the Rhombic form with a marked change of volume at the transition point

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[1] Von Weimarn " *Kolloid Zeitschrift* " Vol II p 81, (1907), has put forward the view that even gases have a micro crystal line structure in their particles According to him all matter is crystalline, and what we call amorphous materials are only so to us, because we cannot see the extremely tiny crystals from which they are irregularly built up

It is difficult to conceive of spherical or ellipsoidal forms having the power to arrange themselves according to geometric laws so soon as the vibrations of heat are reduced to a certain degree, and in the absence of any other directive force so far as is at present known, but if the atoms themselves have definite geometric forms, then arrangement in an orderly space-lattice, so as to produce definite geometric figures peculiar to each atom, appears to be the natural result of the withdrawal or reduction of the vibrations of heat

It should be borne in mind that in Nature the permanent spheroidal form is either the product of living agencies or of rotational movements, and is never associated with matter in its elementary state

The heavenly bodies owe their shape to their rotation around their axes   The fruits and seeds of the Earth are the products of vegetation, and the rounded forms of organic life on sea and land are again the result of living energy   The rounded forms of the pebbles on the sea shore are the result of the ceaseless movement of the waves   Drops of water and other liquids owe their shape to the movement of the drop in passing through the air, and cannot permanently retain the spheroidal form

Geologists are familiar with rounded and spherical forms, but these when carefully considered will generally be found to arise either from organized living forms of past ages, or to meteorites which have fallen upon the earth's surface, and which attained their

spherical shape when in a molten condition by rapid
transit, and probably by a rotational movement

Atoms when in a gaseous state, and rotating rapidly,
will occupy a sphere of influence which will assume a
spheroidal or ellipsoidal form, but the atoms themselves,
when at rest, must be considered in the light of the
crystals which they then form, and must have such
forms as will enable them readily to build up the space-
lattices of their own particular crystals   The crystals
thus formed will not necessarily coincide in form with
the atoms of which they are built up, but may differ
entirely from the form of the atoms of which they are
composed

Consider also the great diversity in the characters
and qualities of the various Elements   Large differences
in melting and boiling points and in other chemical and
physical qualities characterize Atoms of Elementary
Substances, whose atomic weights are in near proximity,
as, for instance, Carbon with atomic weight 12 and
Nitrogen with atomic weight 14

It is generally conceded that we must assume one
general substance as the basic material out of which all
atoms are constructed, and if that be so, it is impossible
to attribute these diversities to difference in essential
character of the material of which they are made up
Taken alone the atomic weights are insufficient to
explain these diversities, and we are consequently led
to look to differences of *form* as the most natural
explanation of this great diversity of character

It would also be difficult to conceive of this large number of distinct atoms each with its own atomic weight, valency, and its group of qualities and affinities, but without form

The Theory of Atomic Form does not exclude the possibility of each atom being constructed of a large number of very small particles or corpuscles, or, as we prefer to designate them, " sub-atoms," which may constitute the " materia prima " out of which all atomic bodies are constituted Such a view would be quite consistent with the arrangement of these sub-atoms so as to form a number of geometric forms, but if such be the case, it seems probable that the sub atoms are in close contact without any interspaces such as we find in the space lattices of crystals A truly solid figure of this class would necessarily have great stability, but might be broken up in a vacuum tube when under the influence of strong electric or other forces

There appears to be great difficulty in reconciling the Electronic Theory of the constitution of the Elements with the considerations stated above The suggestion that the atom is a system of negatively charged corpuscles revolving around a positively charged centre cannot readily be reconciled with the power which each Element possesses of building up its own crystalline form with its great stability, sharp edges and smooth faces Such a conception of atomic structure appears to be at variance with our knowledge of crystal structure, and fails to assist us with the many problems of organic chemistry by which we are still confronted

According to a recent publication by Stewart, the
Electronic Theory has not been generally adopted by
organic chemists, he writes [1]

> "It seemed as though the discoveries in Elec
> tronic Physics would have their reaction upon our
> structural views, but though several attempts have
> been made in this region of the subject, Organic
> Chemists in general have not welcomed them with
> anything like whole-hearted encouragement   There
> is a feeling apparently that in abandoning the usual
> structural formulæ and replacing them by elec-
> tronic symbols, the subject is being complicated
> instead of simplified, and this feeling, whether it
> be due to scientific caution or to mere conservatism,
> has certainly carried the day for the present"

It is suggested that until the electronic constitution
of matter is brought more into accord with the phenom
ena of Organic Chemistry, we are at liberty to consider
any other theory that seems likely to assist in the
solution of the problem

The task of assigning definite geometric form to
each Element and agreeing such form with the known
atomic weights, valencies and other characters of the
element, is surrounded with many difficulties   At pre-
sent we propose to consider only the element Carbon,
which, by reason of the extraordinary number and
variety of its compounds, reveals its character more than
any other atom, but in the first place we offer a few
words on the possibility of designing a geometric form
suitable for mono valent and di-valent Elements

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[1] Stewart—"*Recent Advances in Organic Chemistry*," (1920),
page 2

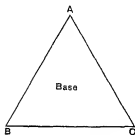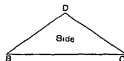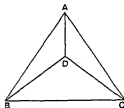Suggested possible form of a MONOVALENT ATOM

Fig 1   Base

Fig 2
One of the 3 sides
surrounding the apex

Fig 3
Stable position attached
by base

Fig 4
Unstable position, attached by
one of the 3 sides meeting
at the apex D

Suggested possible form of a DI-VALENT ATOM

Fig 5
Base of Prism

Fig 6
Sides of Prism

Fig 7
Form of Prism with triangular
Base as above
If the base be enlarged the sides
will be longer and narrower

A possible model of a Hydrogen Atom can be pre-pared, see Figs 1 to 4   The form is a very oblate pyramid with a base smaller than the face of the carbon atom   It can form stable attachment with Carbon or Oxygen, etc , *only by the base*, but that is large enough to prevent the attachment of any other Element   Two such figures, united by the base, form a small but compact figure which might represent a molecule of Hydrogen Gas, and in that condition it will not readily unite with any other Element

A model of a di valent Atom can also be prepared See Figs 5 to 7

When submitting these figures it is to be clearly understood that they are merely guess-work efforts, much more study and research being necessary before the true forms can be established, but they are intend-ed to shew that models of mono- and di valent atoms are not impossible

It will be asked, how can the suggested hypothesis of Atomic Form be reconciled with the present theories of Valency ?

It is suggested that Valency consists of the ability of an Element to attach itself to other atoms either of the same or some other Element and is dependent upon the number of faces of its geometric figure, which are available for making stable attachments No solid figure can have less than four faces, but it may be of such a form that only one, or it may be, two of its faces are so situated or of such a size and shape as to be capable of forming a stable attachment

Moreover, in each particular case, the possibility of such an attachment must depend upon other conditions, namely, the form of the atom to be attached and the relative movements of the two atoms and their axis of rotation, if in the gaseous condition

A great amount of study and research will be necessary in order to design forms which shall comply with the known requirements of the doctrine of Valency, but it is contended that such forms can be designed and the requirements met

The so-called "*double bond*" between adjoining Carbon Atoms deserves special notice There appears to be no definite evidence that the Carbon Atoms are really united by a double or treble linkage On the contrary, the carbon chain breaks more readily at this point than elsewhere, and the carbon compounds containing a so called "*double bond*" readily take on additional atoms or groups The term "*double bond*" is, in reality, a "*figure of speech*" which expresses the fact that two unsaturated valencies exist in regard to two adjoining carbon atoms

It is submitted that the form of the carbon chain and its rotational movement fully account for the occurrence of such unoccupied faces in *pairs*, and generally on adjacent carbonoids The matter will be more fully dealt with in Chapter V , under the heading of " Law of even numbers," and in Fig 26, page 38a, where the pairs of faces are shown

These observations refer to carbon compounds where the unsaturated valencies of adjoining Carbons are held to satisfy one another, such as Ethylene and Acetylene, but there are other cases where "*double bonds*" are held to exist between Oxygen and Carbon, as in the Aldehydes and Acids

These cases are peculiar by reason of the fact that so long as di-valent oxygen is in the form of a hydroxyl group, and has only one free valency, it functions towards Carbon as a mono valent atom, but if the hydrogen be removed from the Hydroxyl, the oxygen is supposed to act as a *di* valent atom, and appears to be capable of satisfying two carbon valencies

It is suggested that the conduct of Carbon, Oxygen and Hydrogen in these positions can only be properly understood when the geometric forms of all the three atoms are known, and their interactions clearly portrayed

The hypothesis of Atomic Form adopts the following conceptions with regard to elementary Atoms, viz

(1) The Atom has a definite geometric form which distinguishes each Element from all others

(2) Atoms belonging to the same group in the Periodic Law differ in magnitude but may have the same or similar forms

(3) The valency of an Element is the number of faces available for stable attachment to other atoms of the same Element or to atoms of some other Element

(4) The geometric form of the atom confers upon it its characteristic qualities and powers

(5) Except at 0° on the absolute scale of temperature all atoms must be considered to be in motion, either vibratory or translatory   In the case of gases the molecules are considered to have both rotational and translatory movement

The adoption of the above conceptions is no doubt difficult, in view of the regularity of the differences of valency and Atomic weight of the groups in the Periodic Table of the Elements, and the similarity of the several increases in atomic weight   This matter will be further considered in Chapter XII, "Concluding Observations"

The remaining chapters of this book will be devoted to the consideration of the possible form of the element Carbon, and an attempt will be made by models of the Carbon framework of various compounds, to shew the agreement between these models and the known facts with regard to the compounds which they represent

CHAPTER II

THE CARBONOID AND ETHYLOID

To attempt the design of a geometrical solid which may fitly represent the Carbon Atom, is a task of considerable difficulty

The universal tetravalent character of carbon compels us to suggest a tetrahedron for the model, but there are a large number of tetrahedra, any one of which might be adopted   In view, however, of the equality of the four valencies we are led to adopt a figure in which all the faces are equal, but we have still a large number of forms available, dependent upon the character of the face adopted   The formation and stability of the Benzene Nucleus suggests that the tetrahedron should be of such a form that six atoms can combine to produce a new figure   Only one figure can now be designed which will fulfil all our requirements

Accordingly, we submit the model, Fig 8, which will be called a carbonoid   Its features are

(1) All the faces are alike in every respect, and stand in the same relationship to one another

(2) There are two equal solid angles, A C and B D in Fig 8, and four other solid angles equal to one another, but differing from the other two, the two equal solid angles are each 1/6th part of four right-angles, so that the angle at E, Fig 8, is an angle of 60°

(3) The faces are isosceles triangles, and they have the peculiarity that the base is equal to the normal to the base   See Fig 9

(4) If the figure be divided into two equal portions by a plane passing through one of the triangular faces, B—D, and also through a point bisecting the opposite solid angle at E, such plane will be an equilateral triangle See Fig 8
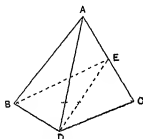

Fig 8   The Carbonoid
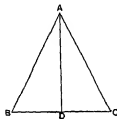B D E is an equilateral Triangle

Fig 9
Face of Carbonoid
A D = B C

It will be admitted that this figure, the " Carbonoid" has some special features—more than the regular Tetrahedron—and it seems impossible to design any other figure which will be so simple and at the same time so symmetrical

If two carbonoids are joined together by any of their faces, a new six-sided figure is produced, which is called an " Ethyloid " See Fig 10, p 14   It differs materially from the carbonoid and from any other combination of carbonoids   There is nothing at all like it among the models which contain three or more

carbonoids   There is now a slight difference in the
position of the faces, which are arranged in pairs   Two
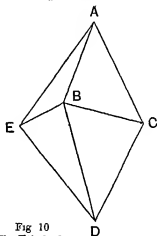pairs are alike in their positions relatively to one another,

Fig 10
The Ethyloid

and to the rest of the figure, viz , A E C, D E C and
A B C, D B C, but the third pair, A B E and D B E, are
differently placed, the solid angle at B E dividing the two
faces, being situated nearer to the centre of the
figure, the line B—E forming the bases of the two
isosceles triangles   This is called a *co basal* pair of faces
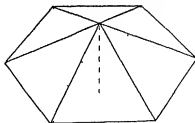
Fig 11
The
Benzenoid

If six carbonoids or three ethyloids are joined together in regular order, a new figure is obtained, called a " *Benzenoid*," Fig 11, which has twelve faces, all exactly alike, and all occupying similar positions in the figure This is a very compact and symmetrical figure, and should have great stability and special features and characteristics separating it from all other combinations of either Carbonoids or Ethyloids

We will consider presently the models of Carbon Chains, in connection with which there are some interesting features, but first let us consider the model of the " *Ethyloid* "

Every Chemist will allow that the Ethylene group occupies a very important position in Organic Chemistry It is the basis of a large number of substances both useful, important and abundant In an homologous series it is the compound containing two Carbons only that usually occupies the most important place in the series Moreover, the *Ethyl* group occupies an important position in a large number of substances and we notice its stability in the Ethers

The importance of this group is shewn by the following Table of Compounds of two Carbons —

Ethane	$C_2 H_6$	
Ethylene	$C_2 H_4$	The principal constituent of Coal Gas
Acetylene	$C_2 H_2$	
Ethyl Alcohol	$C_2 H_5$ OH	The Alcohol of Commerce
Acetaldehyde	$C_2 H_4$ O	

Acetic Acid	$C_2 H_4 O_2$	The commonest monobasic acid
Oxalic Acid	$C_2 H_2 O_4$	The commonest di-basic acid
Di-ethyl Ether	$C_2 H_5 O C_2 H_5$	The commonest Ether
Cyanogen	$C_2 N_2$	

The Ethyloid is more convenient in shape than the Carbonoid and far exceeds in symmetry and compactness all the other groups It should have great stability It is significant that this form coincides with a group so widely known and of such general usefulness, and occupying such an important position in Organic Chemistry

The position of the acids of two Carbons only is further shown by considering the Diagrams of melting points of the monobasic and di-basic acids, which are given in Holleman's "Organic Chemistry", Fifth Edition, pages 106 and 199 In these two Diagrams the lowest melting point coincides with a chain of 5 carbons, there being a remarkable fall between the acid containing 4 and that containing 5 carbon atoms Throughout the two series there is a fall as we pass from even to odd numbers, and a marked recovery on returning from odd to even Another remarkable feature is the high melting-point of the acid containing two carbons only Some of the figures are now given

	Monobasic Acid	Di basic Acid
One carbon	+ 8 3	
Two carbons up	+ 16 7°	+ 189 5

		Monobasic Acid	Di basic Acid
Three carbons	down	— 22 °	+ 133 0
Four ,,	up	— 3 1	+ 183 0
Five ,,	down	— 58 5	+ 97 5
Six ,,	up	— 1 5	+ 153 0
Seven ,,	down	— 10 5	+ 105 5
Eight ,,	up	+ 16 5	+ 140 0

In the case of the Paraffin Series where there is no acid radicle attached, the lowest member of the series contains only three carbons See Diagram Fig 12, p 18 The anomalous position of the compound containing two carbons is, however, continued in this Diagram, thus confirming the unique position occupied by all compounds of two carbons only, which is associated with the form of the Ethyloid

It is noticeable also that the special form of the Ethyloid is associated with a high melting point, and there is reason to believe that compounds of symmetrical and compact form are distinguished by higher melting points

In Stewart's *Stereochemistry*,[1] the following statements are made

"In 1882 Carnelly stated that of two isomers, that which possessed the most symmetrical and compact structure was distinguished by having the higher melting-point and Franchimont has brought evidence in favour of this view

Werner puts forward the idea that this one difference in melting-point may be merely one instance of a much more general rule"

[1] Stewart—"*Stereochemistry*," (1907) pp 174/5
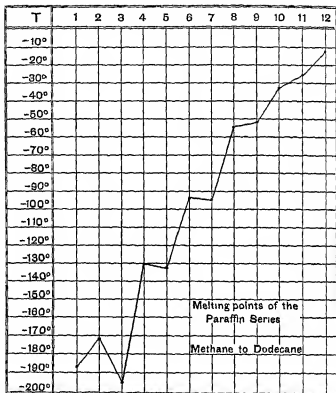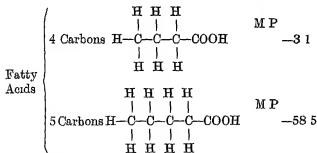
NUMBER OF CARBON ATOMS

T	1	2	3	4	5	6	7	8	9	10	11	12
−10°												
−20°												
−30°												
−40°												
−50°												
−60°												
−70°												
−80°												
−90°												
−100°												
−110°												
−120°												
−130°												
−140°												
−150°												
−160°						Melting points of the						
−170°						Paraffin Series						
−180°						Methane to Dodecane						
−190°												
−200°												

Fig 12

In this Chart, the compound containing 3 carbons has the lowest melting point In the Fatty and Dı basic Acids there is a heavy fall between 4 and 5 Carbons, and the compound containing 5 carbons is by far the lowest of the series

"This idea may prove to be based upon mere coincidence, but the fact that benzene para-derivatives have higher melting points than the corresponding ortho-derivatives seems to point to some general rule such as Werner foreshadows"

In the Second Edition, under "*The properties of Ethylene Stereoisomers*"[1]

"Carnelly's rule that the higher melting-point is generally associated with symmetry and compactness of structure finds an illustration in the fact that axially-symmetrical ethylene isomers have melting-points higher than those of the plane-symmetrical type   They are also less soluble and less volatile, and they appear to have higher densities"

The Theory of Atomic Form receives some confirmation from the differences of melting points between those acids containing an even and those of an uneven number of carbon atoms   If the carbon atom be supposed to be a sphere or cube it is difficult to understand why such large differences should exist, thus —

	H H H	M P
4 Carbons	H—C—C—C—COOH	—3 1
	H H H	

Fatty
Acids

	H H H H	M P
5 Carbons	H—C—C—C—C—COOH	—58 5
	H H H H	

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[1] Stewart—"*Stereochemistry*," 2nd Edition, (1919), p 118

If four Carbons are represented by four spheres and an additional sphere is introduced into the Carbon Framework of the Acid, producing a *fall* in the melting point of 55°, it is inconsistent that the introduction of a further sphere should produce a *rise* in the melting point of 57° to −1·5°

When, however, the chain of carbonoids is inspected, see Fig 26, p 38a, we see that the introduction of an additional carbonoid produces considerable change in the position of the end carbonoid to which the acid radicle is attached, the effect of this alteration being to reverse the position relatively to the rest of the chain of the end carbonoid, and the attached acid radicle   This change may well be sufficient to alter materially the relationship between the carbon chain and the acid radicle, and thus give rise to a change in the properties of the substance

It will be seen that the differences of melting points are much larger in the case of the Acids than they are in the diagram of the Paraffin Series, shewing plainly the effect of the Acid Radicle, but these differences persist in the case of the Paraffin Group, indicating that the cause of the differences in character is to be found in the Carbon Chain, and that the function of the Acid Radicle is to enhance the effect of this peculiarity   An important feature of the Carbonoid Chain is the change in the position of the end Carbonoid taking place at each change in the number of carbons in the chain, with a more or less marked reversion to the old positions when we get back to the corresponding odd or even number of carbons

This may furnish us with an explanation of the variations in melting points of these compounds

CHAPTER III

BENZENE AND SOME OF ITS DERIVATIVES

The Benzenoid, Fig 11, p 14 is a completely symmetrical figure and admits of no division into right-handed and left-handed isomers—optical activity, such as arises when asymmetry exists, is therefore impossible

Among Benzene derivatives it is generally the case that all those which do not involve the existence of an attached chain of two or more carbonoids (added to the Benzenoid at the same point) are inactive, and the Benzene Ring, with the addition of a single atom, other than Carbon, will also be inactive, thus

I INACTIVE   II POSSIBLY ACTIVE

CH_3 in I is attached to the Ring so as to be not in the plane of the paper but at right angles thereto, and in No II CH occupies a similar position CH_3 in No 2 is again approximately in the plane of the paper, and may be on the right hand or the left See Fig 13, p 22, A and B representing the enantiomorphous forms of the two isomers
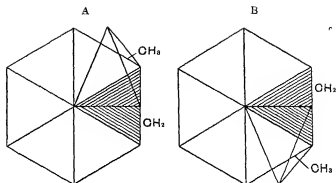
Fig 13

The two isomers of No II cannot be made to corres-
pond   In one of the isomers the C H$_3$ group will be
on the side nearer to the O H group, and in the other
it will be on the other side and further from the hydroxyl

This Form is described as "*possibly*" active, because
if the carbonoids forming the chain are differently
arranged, no right and left-handed isomers will exist,
the arrangement being symmetrical, thus
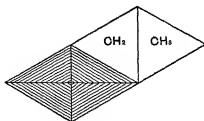
Fig 14
Perpendicular View
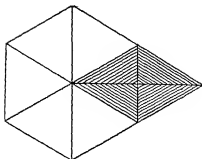
Fig 15
Horizontal View

These facts concerning the inactivity of Benzene and its derivatives are borne out by experimental data In Cohen's "*Organic Chemistry*," it is stated that there is no asymmetry in Benzene and no optical enantiomorphs[1]

> "All attempts to resolve Benzene Compounds have been fruitless, and what is even more significant, there is no single instance of an optically active compound of Benzene, among the many derivatives found in Nature, which owes its activity to the asymmetry of the nucleus"

It is not only necessary to produce a model of six Carbonoids which will correspond with the known characters of Benzene, such as the entire absence of enantiomorphism of the molecule, and the fact that only six out of the twelve faces are occupied by Hydrogen

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[1] Cohen—*Organic Chemistry*, 1st Edition, p 446

It is assumed that the figures of Carbon and its compounds when in the gaseous state are floating in a medium which supports them in much the same way as water supports any objects floating in it, and that the molecules are subject to the same laws of gravity and mutual attractions as are observable in other and larger objects   If it be allowed that the Hydrogen Atom has the form of a very oblate pyramid, it will follow that nascent Hydrogen will adopt a position in which the base of the pyramid will be above and the apex will occupy the lower position thus

Base

Apex
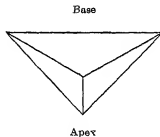
Fig 16

In this position the Hydrogen Atoms will readily combine with the lower surface of the Benzenoid, but it will be practically impossible for them to make stable attachments to the upper surface, to do so it would be necessary for the Hydrogen to make a complete inversion of its position so that the base may be below and the apex above, such a change of position would be unlikely   In this view, it would be the *upper* surface of the Benzenoid which would be free from Hydrogen

It may be argued that if the Hydrogen Atom was so placed as to be unable to attach itself to more than one side of the Benzenoid, would not this fact also prevent the union of two Hydrogen Atoms to produce a molecule of Hydrogen Gas, but it will readily be seen that in such a combination we have two atoms of Hydrogen concerned, both of which would be disposed to move towards each other and only one half of the inversion of each atom would be necessary to enable a stable union between the two atoms to take place by attachment of their bases

When the Benzene Nucleus is formed by the coming together of three Ethyloids, freed from Hydrogen, an atmosphere of nascent Hydrogen will surround the Benzenoid, and the under surface thereof may be supposed to obtain immediate attachment of Hydrogen, but the upper surface may remain free to form attachment to other atoms if such are in a nascent condition and occupy suitable positions   The subsequent conduct of the Benzene Nucleus may depend upon the character of the atom with which it is brought into contact, and the circumstances such as heat, pressure, etc, existing at the time, together with the peculiar movements rotational and otherwise of both groups relatively to one another

BENZENE DERIVATIVES

Certain syntheses which assists the hypothesis of Atomic Form, are those of certain derivatives of Benzene *Trimethyl Benzene* 1 3 5 or *mesitylene*, can be produced from three molecules of Acetone on treatment with sulphuric acid

Acetone

$$\begin{array}{c} H \quad O \quad H \\ | \quad \; | \quad \; | \\ H-C-C-C-H \\ | \quad \; | \quad \; | \\ H \quad \quad H \end{array}$$

less $H_2O=$

$$\begin{array}{c} H \\ | \quad | \quad | \\ H-C-C-C-H \\ | \quad | \quad | \\ \quad \quad H \end{array}$$
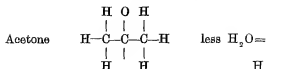
three molecules of which when
nascent give

mesitylene
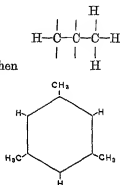
     The model of the Carbon Framework of mesitylene,
and the condensation of 3 Acetone molecules to produce
Mesitylene, are shewn in Figs 17 and 18, p 25a, and it
will be seen that its configuration is such that the three
molecules of Acetone unite together so as to produce
the Benzene Derivative without any change in the posi-
tion of the carbons, or any break of the carbon frame-
work   Any chain consisting of cubes or spheres or
similar bodies would have to have a configuration

$$O-O,$$

or else the position of the carbon atoms would have to
be changed, and the chain broken in order to enable the
Benzene nucleus to be formed   The chain of Carbonoids
in Acetone is so formed as to be able (after the loss of
H_2 O) to form one-third of the Benzene Derivative with-
out any alteration
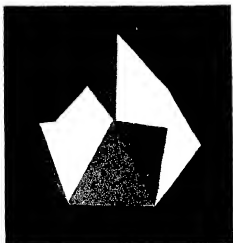
MESITYLENE
Fig. 17
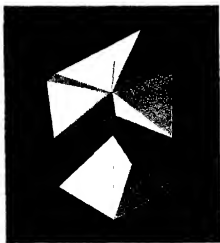
Union of 3 ACETONE MOLECULES to form MESITYLENE
Fig. 18

A similar case is that of the synthesis of *Triacetyl Benzene* 1 3 5 from three molecules of *Aceto-acet-aldehyde*.
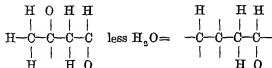
three molecules of which make *Triacetyl Benzene* 1 3 5
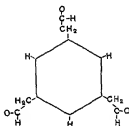
In this case the models shew that the Benzene Derivative is formed without bending or breaking the Carbon Chain.

Again, three molecules of *Dimethyl Acetylene*
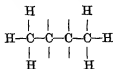
will produce *Hexamethyl Benzene*

C

In this case the molecule of the Dimethyl Acetylene must be of such a form that the atoms of CH_3 will appear on the same side of the Benzene nucleus, thus

$$C_{12} \quad H_{18}$$
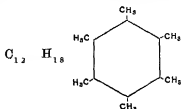
Dimethyl Acetylene must therefore have the form

$$
\begin{array}{cc}
CH_3 & CH_3 \\
| & | \\
-C & -C- \qquad A \\
| & |
\end{array}
$$

The two CH_3 groups are evidently added to the opposite ends of the Acetylene group There are two ways in which two single carbonoids can be added to an Ethyloid

$$
\text{Either} \quad
\begin{array}{cc}
CH_3 \\
| \\
-C-C- \\
| & | \\
CH_3
\end{array}
\quad \text{or} \quad
\begin{array}{cc}
CH_3 & CH_3 \\
| & | \\
-C-C- \\
| & |
\end{array}
$$
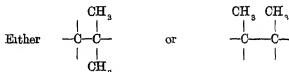
One is as likely as the other   We are, therefore, entitled to select the formula, the carbon framework of which is given above, A

Three of these molecules can readily combine to form a Benzene Nucleus plus six groups of CH_3 on the same side of the ring as already shewn above, without any change in the configuration of the carbon chain or any breaking of the chain

Another interesting case of a similar character is
the condensation of di acetyl to form p xyloquinone
On removing one molecule of water from each mole
cule of di-acetyl we have

$$
\begin{array}{cccc}
\text{H} & & \text{O} & \\
| & | & | & | \\
\text{H—C—C—C—C} & & & \text{H} \\
| & | & | & \\
\text{H} & (2) & (3) & (4) \\
(1) & & &
\end{array}
$$
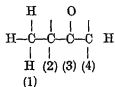
Here the three carbonoids Nos (2), (3) and (4) are
so arranged that they form one-half of a Benzene ring
presenting a *co-planar* face consisting of one face of
each of the two carbonoids C(2) and C(4) see Fig 45,
p 72a   On removal of H_2O these co-planar faces are
unsaturated and immediately unite to form

p zyloquinone
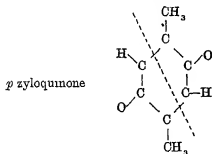
Here again the models shew a remarkable facility
for the formation of the Benzone derivative

Fig 19

Ring of 60 carbonoids, or 6 rings of 6 carbonoids
each, and 6 links of 4 carbonoids each

CHAPTER IV

THE ALLOTROPIC FORMS OF SOLID CARBON

Pure Carbon exists in three forms   Diamond,
Graphite, and Amorphous Carbon   The production of
amorphous carbon proceeds on the following lines
If Benzene is passed through a glowing tube Naph-
thalene $C_{10} H_8$ and Pyrene $C_{14} H_{10}$ are produced
On heating Naphthalene or Pyrene to a *still higher
temperature*, in absence of air, amorphous carbon results

What number of carbon atoms are there in amorph-
ous carbon and what is the form of the molecule ?
There is strong ground for concluding that there are
several rings of six carbons and that there is a large
number of carbon atoms in the molecule

In Fig 19 we shew a ring of 60 carbonoids
which is capable of indefinite extension and which may
very well stand for a molecule of amorphous carbon

When a lamp smokes the air is filled with little
specks of amorphous carbon each of which will be made
up of many thousands of these groups loosely held
together   If, however, pure Carbon is formed under
suitable conditions Graphite may be produced, but very
high temperature and great pressure is needed to produce
the Diamond   It is doubtful if Graphite can be con-
sidered as crystalline in formation, but it has *some* of
the characteristics of a crystal

If the structure here shewn is extended in all directions, a network is formed as shewn in Fig 20, and this network may, under suitable conditions, extend in all directions in the same plane   Such a network may be fractured, and the line of fracture will be as shewn by the black lines on the figure   It will be seen that the lines of fracture form equilateral triangles

Now let us look at a photograph of a piece of Graphite as seen through the microscope, Fig 21, p 30b   There are a number of lines clearly marked, and it is clear that these lines are all arranged relatively in the same way as the sides of an equilateral triangle It is suggested that they represent the lines of fracture of a network of carbonoids as shewn in Fig 20

In support of this statement we may refer to the synthesis of Mellitic Acid by the oxidation of graphite or wood charcoal   Assuming that Graphite has the structure shewn in Fig 20, viz,
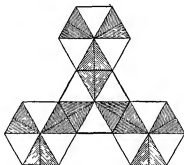
the lines of cleavage will be as shewn by the heavy line giving molecules of the following type and *leaving no residue*
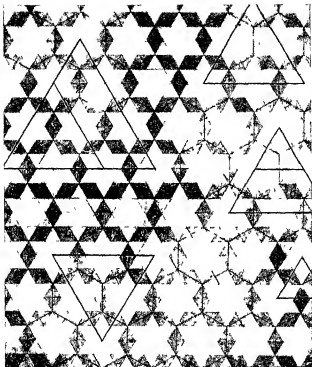
Fig 20

Network consisting of the extension in all directions in
the same plane of the Rings of 60 carbonoids, showing
the Lines of Cleavage

$$(a) C \quad \begin{matrix} C \\ \diagup \quad \diagdown \end{matrix} \quad C (a)$$
$$C \quad C$$
$$(b) C \quad C \quad C (b)$$
$$C$$
$$C \quad C$$
$$(a) \quad (b)$$

a   above

b   below
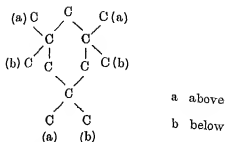
This accords with the assumed character of the car-
bonoid network, and would give the following formula
for mellitic acid

A (a) HOOC   C   COOH (a)
    C   C
    (b) HOOC   C   C   COOH (b)
    C
    HOOC   COOH
    (a)   (b)
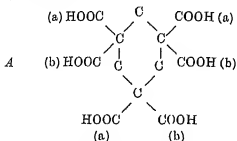
The usual formula for Mellitic Acid is

    COOH
    |
    C
HOOC—C   C—COOH
HOOC—C   C—COOH B
    C
    |
    COOH
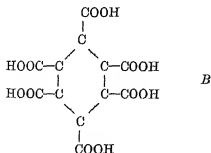
We have not been able to ascertain the evidence on which this formula is assigned to Mellitic Acid, and it seems possible that formula " A " may be correct

There are other facts associated with the reactions connected with Mellitic Acid which indicate the probability that formula " A " is preferable to formula B If this be the case, the form of the carbonoid network shewn in Fig 20, p 30a is confirmed

The Diamond crystallizes in the form of a regular Octahedron or more rarely the cube, but these are compound figures   The simplest form of the Diamond is a tetrahedron, not the irregular tetrahedron of the carbonoid, but one that could be used for either an octahedron or a cube, the base is an equilateral triangle, and the three other sides are right angled triangles

If a few models of the tetrahedral form are made, they can be combined so as to form both the octahedron or the cube, and it will be seen that the three sides surrounding the apex of the tetrahedron will correspond with one half of the sides of the cube, the apex being the corner of the cube , and they will present an arrangement of squares while the base of the tetrahedron will present the appearance of equilateral triangles, and will correspond with the faces of the octahedron   Uncut stones are obtainable in all three forms, the tetrahedron, the cube and the octahedron

The base of the tetrahedron and the faces of the octahedron are adorned with equilateral triangles representing the positions where a layer of the substance of the Diamond ends   Some photographs of the appearance of the face of the natural Diamond

Fig. 24
DIAMOND
Base of TETRAHEDRON   Objective 1″
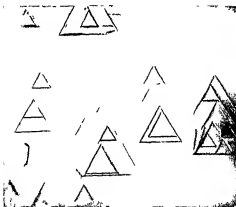
Fig 25
DIAMOND
Face of OCTAHEDRON   Objective ½″

are now given, Figs 22 and 23, and 24 and 25, and we see here the same formation which we saw in the case of graphite clearly portrayed

It will be seen in Fig No 24 that the equilateral triangles are arranged in a position opposite to that of the triangular face of which they form a part, the bases of the triangles of the fractural markings being in the direction of the apex of the triangular face If, however, the face of the Diamond be exposed to a high temperature under the oxyhydrogen blow-pipe, a portion of the surface is removed and a new set of equilateral triangles appears with their bases inverted so as to correspond in position with the triangular face of which they form a part

On reference to Fig No 20, p 30a it will be seen that the lines of fracture can be drawn in two different ways, either base above or base below, in this respect therefore the network of carbonoids is able to depict the natural phenomenon exhibited by the faces of the Diamond

Dr Max Bauer, writing on the structure of the Diamond, says

> "The Triangular pits are regular pyramidal depressions of which the bases are equilateral triangles They are usually small and often only to be seen distinctly under the microscope
>
> "These depressions are of the same general character as those produced on the octahedral faces of a diamond during its combustion, but while the corners of the pits are of natural origin are adjacent to the octahedral edges, this position is occupied by the *sides* of the pits produced by etching, thus the two positions are the reverse of each

other   The pits occur singly or in large numbers, and the striations may or may not be also present on the same face "[1]

So far we have only arranged the carbonoids so as to produce a network with equiangular lines of fracture Can a space-lattice be built up to correspond with the structure of the Diamond ? This can be done, but the number of carbonoids employed is so enormous that we have been compelled to resort to the use of hexagonal cards to represent the Benzene nucleus   In this way a model has been prepared which corresponds with the form of the tetrahedral Diamond   It will, however, be very difficult to include a photograph of this model in the illustrations by reason of the large size of the model required to shew the tetrahedral figure and the enormous number of cards which are required for its construction

It is claimed that the capacity of the carbonoid to build up models of all the forms of solid carbon has now been shewn, but the illustrations fail to display fully the agreement between the models and the different forms of Diamond, this can best be seen by consulting the models themselves

NOTE —*27th January*, 1922

At the meeting of the British Association in Edinburgh, September, 1921, a Discussion took place on the Structure of Molecules—opened by Dr Irving Langmuir   In the discussion which followed, Prof

[1] *Precious Stones*, Max Bauer, 1904, page 124

W L Bragg, after considering the structural form of
Calcium Carbonate as revealed by X-ray analysis, is
reported to have said

> " The interpretation of the Structure of
> Graphite is not quite so certain as that of calcite,
> but the evidence is very strongly in favour of a
> *hexagonal arrangement in sheets*

> " Each carbon atom is equally related to three
> neighbours in the same plane   They are separated
> by a much greater distance from the atoms in other
> planes, and the cleavage indicates that the forces
> between successive planes are slight   These
> hexagons might be written as Benzene Rings with
> Valency Bonds, but such a formula would indicate
> a lowered symmetry of the structure, which is not
> the case "

CHAPTER V

LAW OF EVEN NUMBERS

The ordinary features of carbon chains are faithfully reproduced by the models, the well known formula C_nH_{2n+2} applies to strings of carbonoids, the available faces corresponding to $2n+2$

We have already considered the Ethyloid with six faces If to this one carbonoid be added the next group of three carbonoids has eight faces, and so on

The models serve equally well for representing the carbon framework of molecules with branched chains

The number of Hydrogen atoms or its substituents attached to a carbon chain is always *even*, in the saturated compounds C_nH_{2n+2} the number of Hydrogen atoms is naturally even, and in the unsaturated substances with the formulæ C_nH_{2n} or C_nH_{2n-2}, the number of Hydrogen atoms is still even, when other elements such as Halogens, Nitrogen, etc, are introduced the number in the molecule by substitution the total carbon valencies occupied remains an even number From this it follows that the unoccupied carbon valencies are always 2 or a multiple of 2

This peculiarity of carbon chains is thus described in Holleman's Organic Chemistry[1] "*Law of the Even Number of Atoms*" The number of Hydrogen

---

[1] Holleman's Text Book of Organic Chemistry, 5th English Edition, pp 47 48

atoms in the saturated hydrocarbons is even, since their formula is C_nH_{2n+2} All other organic compounds may be regarded as derived by exchange of these Hydrogen atoms for other elements or groups of atoms, or by the removal of an even number of hydrogen atoms or by both causes simultaneously From this it follows that the sum of the atoms with uneven valency (Hydrogen, the Halogens, Nitrogen, Phosphorus, etc), must always be an even number The molecule of a substance of the empirical composition $C_3H_2O_3N$ must be at least twice as great as this, because $2H + 1N$ is uneven "

The following instances may be quoted —

C_2H_4 Ethylene

$$
\begin{array}{cc}
H & H \\
| & | \\
H\!-\!C\!-\!C\!-\!H \\
| & | \\
\end{array}
$$

C_2H_2 Acetylene

$$
\begin{array}{cc}
| & | \\
H\!-\!C\!-\!C\!-\!H \\
| & | \\
\end{array}
$$

$C_3Br_3H_5$ Tri bromo-propane

$$
\begin{array}{ccc}
H & H & H \\
| & | & | \\
H\!-\!C\!-\!C\!-\!C\!-\!H \\
| & | & | \\
Br & Br & Br \\
\end{array}
$$

on removal of H Br we get

$C_3Br_2H_4$ Di bromo-propane

$$
\begin{array}{ccc}
H & & H \\
| & | & | \\
H\!-\!C\!-\!C\!-\!C\!-\!H \\
| & | & | \\
& Br & Br \\
\end{array}
$$
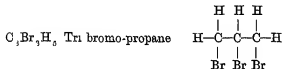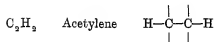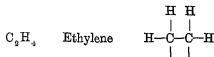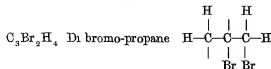
on removal of 2Br there remains

$$C_3H_4 \quad \text{Allene} \quad \begin{matrix} & & H & & \\ & | & | & | & \\ H-&C-&C-&C-&H \\ & | & | & | & \\ & & H & & \end{matrix}$$
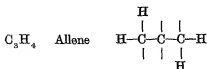
If an attempt be made to satisfy the unoccupied valencies shewn, the molecule will take up Hydrogen, Chlorine, Bromine, Iodine, Oxygen, or other atoms, but so as *not to leave an uneven number of faces vacant*

This Law is due mainly to the character of the carbon chain, and must be attributed to some peculiarity of its configuration   No satisfactory explanation has, hitherto, been put forward

We will presently consider the three pairs of faces exhibited by the Ethyloid   A similar arrangement of pairs of faces exists in the Tri-carbonoid and all the compounds represented by higher numbers of carbonoids

A photograph of a chain of 17 carbonoids, is here given and the arrangement of the faces in *pairs* may be easily seen , see Fig 26   The following characteristics should be noted —

(1) The number of faces available is 36 $(2n+2)$

(2) The whole of these faces are arranged in pairs, viz 16 co-basal pairs and 2 pairs at each extremity of the chain   In this case the pairs (except the two pairs at the extremities) belong to *adjacent* carbonoids

Fig 26

CHAIN OF CARBONOIDS

A co-basal face is one in which the bases
of the two isosceles triangles are united, thus —
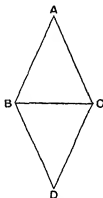
Fig 27
Pair of Co Basal Faces
Base B—C

(3) The faces may also be arranged differently according
to pairs of *concave* faces there being 15 concavities
of two faces each = 30, + 3 odd faces at each
extremity of the chain   These pairs (excepting the
three at each extremity) belong to *alternate* car-
bonoids 1-3, 2-4, 3-5, etc

(4) The two pairs of faces at each end of the chain
occupy special positions which correspond in all
respects to their fellows at the other end of the
molecule, they appear generally to retain their
attached atoms as in the cases of Acetylene and
Allene already mentioned   This may be due to
the fact that the attractive force at the two ends

of the chain will be greater than in the middle, as it will operate most powerfully in the direction of the longer axis   Exceptions may be noted in the case of Cyclo-Propane and other cyclic compounds

The position of the pairs at the extremities of the chain will be changed relatively to the rest of the chain, and relatively to one another, as the number of carbonoids in the chain increases, and as we pass from odd to even and even to odd, such changes of position will be enhanced by any other atoms attached to these faces as in the case of acids referred to in Chap II , and they must affect materially the properties of the molecule   The addition of one carbonoid to the chain has the effect of *reversing* approximately the direction in which the pair of faces at the end of the chain is pointing

It is suggested that in all normal carbon chains, the atoms of Hydrogen, etc , which are in attachment, occupy the two sides of the co-basal pairs of faces, and that the axis of rotation of the molecule will be that which corresponds most nearly with the longer axis of the chain   Any increase in the rapidity of the rotation will tend to throw off the attached atoms in pairs, since if one element of the pair is removed the stability of the other member of the pair will be simultaneously affected, in a similar manner, and to the same extent, and will be removed at the same time   The effect of centrifugal force will be to drive the atoms towards the solid angle separating the co-basal pair of faces where they will meet, and further movement by either atom should be retarded or stopped   When the

rotation is enhanced and the centrifugal force becomes
sufficiently strong, both atoms will be removed at the
same time

Similarly, in an atmosphere of nascent Hydrogen—
if one side of the pair of faces is occupied, there will be
created a position of stability on the other side of the
solid angle which will be occupied by the nascent Hydro-
gen available, or failing such occupation, the single
Hydrogen alone will be unable to retain its position

It will be seen that the two co basal faces belong to
two *adjacent* carbonoids, thus agreeing with experi-
mental data, and accounting for the phenomenon that
when Halogens are removed from the molecule they
take with them a Hydrogen atom from the *adjacent*
carbon atom and not from the one to which the Halogen
is attached   This peculiarity is shewn in the case of
normal Propyl Iodide and Isopropyl Iodide, the models
of which are shewn in Fig 28, A and B

Normal Propyl Iodide   Isopropyl Iodide
CH_3—CH_2—CH_2I CH_3—CHI—CH_3
A   B
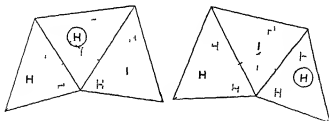
Fig 28

Note   The letters in dotted lines, represent the atoms attached
to the remoter sides of the figure

D

The Hydrogen which leaves the molecule along
with the Halogen is enclosed in a ring, and the illustration
shews that the Hydrogen is much more accessible to
the attraction of the Iodine atom than the atom of
Hydrogen on the *same* carbonoid which is at the other
side of the molecule

THE ETHYLOID

This Law of Even Numbers is well illustrated by
the Ethyloid   When Ethane is passed through a heated
tube it loses two Hydrogen Atoms with the production
of Ethylene C_2H_4

The model of the Ethyloid presents three pairs of
faces, one of which is a pair of co-basal faces   see
Fig 29   The solid angle at B—C which divides these
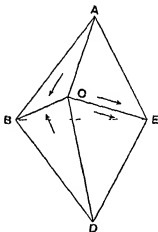
Fig 29
Ethyloid

two faces occupies a medium position with regard to
the Axis of Rotation and the two faces will have an
equal retaining power on either side, there will be no
tendency to drive off an attached atom to the right or
left, see Fig 29   The effect of centrifugal force
upon any Hydrogen attached to these two faces will be
to drive the two attached Hydrogen atoms towards
the base B—C, where the force operating upon each of
the two Hydrogen atoms being equal, and the directions
opposite, they will meet and retard one another from
further movement

The effect of this (coupled with the position of the
axis of rotation) will be that they will probably be
the last to leave the molecule   This is important,
as so long as this pair of Hydrogen is retained, the
molecule is unable to join with other similar Ethyloids
and produce a Benzene nucleus

Of the other two pairs, they may be chosen in
two ways—either two faces on the *same* carbonoid or
two faces on the adjoining carbonoids   The latter seems
the most probable, for the solid angle separating the
pair of faces of adjoining carbonoids is very obtuse,
while that separating the pair on the same carbonoid is
acute   A reference to the model of the Ethyloid,
Fig 29, will shew that the two faces of the adjoining
carbonoids are very close together   With regard to
these two pairs of faces which are not co-basal, a careful
study of the Ethyloid shews that the effect of centrifugal
force upon an attached Hydrogen atom will probably be
to drive it in the direction shewn by the arrows in figure
Fig 29 until it reaches the solid angle at A—E—D   this
is an acute solid angle, where there will be little if any

obstruction to prevent it from passing off the Ethyloid
The axis of rotation of the Ethyloid will no doubt be
determined by the position of its centre of gravity, and
will be nearer to the co-basal faces than it will be to
the other two pairs of faces, so that the point E,
(Fig 29) will have a slightly more rapid movement than
the line B—C, and it will be the point where col-
lisions with other molecules will take place   If these
views are adopted we can see a reason why the Hydro-
gen attached to these two pairs of faces will be thrown
off by the increasing rotation of the molecule, in prefer-
ence to the Hydrogen attached to the pair of co-basal
faces

These two pairs may be distinguished from each
other by the question of whether they lead or follow the
rotation of the Ethyloid   Whether the pair which
follows the Ethyloid will be more easily lost than the pair
which *leads* is a question on which there may be some
doubt, but it is clear that there will be a difference
between the two positions, and one pair will be cast off
more easily than the other   As the rapidity of the
rotation increases, it may be that one pair will be
liable to become detached by collisions with other
Ethyloids   In this way, Ethylene C_2H_4 will be pro-
duced

On passing Ethylene through a red hot tube the
rapidity of the rotation of the molecule may be increased,
with the result that another pair of Hydrogen will be
lost, and Acetylene will result

So far the removal of Hydrogen has not facilitated
the formation of a Benzene Ring, but on further treat-
ment with heat the last pair of Hydrogen is driven off

from the co basal pair of faces and the Ethyloid unites
with two other similar molecules to form a Benzenoid,
thus —
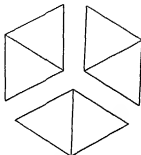
Fig 30

It is interesting to observe that it is only on the
removal of the last pair of Hydrogen Atoms that the
formation of Benzene takes place, and that the peculiar
formation of the Ethyloid seems to necessitate that the
co-basal pair will be the last to leave the molecule

Throughout it has been assumed that the Ethyloid
has a rotational movement around an axis passing
approximately through the centres of the two carbonoids
This seems to be inevitable   The Ethyloids, under the
influence of a high temperature, must also have a
translatory movement, and collisions will probably occur
frequently   The effect of such collisions on a spherical
body would be the production of a spin in one or both
of the colliding molecules, and in the case of the Ethyloid
it is difficult to conceive of a collision taking place
without the production of a rotational movement in
both molecules which will increase in rapidity with any
rise in the temperature

THE TRICARBONOID

The Tricarbonoid has 4 pairs of faces, two co-basal pairs, one on the front of the model and one on the back, marked A_1 and A_2, and B_1 and B_2 There is also one pair of opposite faces occupying the faces of the concave side marked C_1 and C_2, and a pair of single faces marked D_1 and D_2, occupying similar positions at the opposite ends of the figure   As shewn in Fig 31
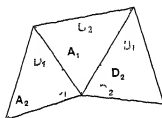
Fig 31
The Tricarbonoid

The tetracarbonoid can be divided into pairs of faces in a similar way, and so on with other carbon chains

THE BENZENOID

This figure cannot be divided into pairs of faces in the same way as the carbon chain   When Hydrogen is added to Benzene, the atoms are attached to the unsaturated faces of the Benzene nucleus in pairs C_6H_8, C_6H_{10}, C_6H_{12} See Holleman's Text Book of Organic Chemistry, First Edition p 355

"When the aromatic hydrocarbons take up two or four hydrogen atoms, they lose their aromatic

character and acquire properties peculiar to unsaturated compounds

" *Dihydrobenzene*, C_6H_8, for example, reacts with a solution of permanganate and sodium carbonate, and also adds on four Bromine atoms

" *Tetrahydro Benzene*, C_6H_{10} readily adds on two Bromine atoms "

The special form of the Benzenoid and the comparatively smooth surface of its unoccupied side must render it very difficult for the first pair of Hydrogen atoms to become attached thereto, having regard to the fact that it must be considered as rotating rapidly around its shorter axis   When, however, one pair of Hydrogen or other atoms is attached, the smoothness of the surface would be disturbed and the addition of other atoms or groups would become comparatively easy   This may account for the change of character which takes place when addition products are made to Benzene and the fact that whenever it takes on two or four hydrogen atoms it acquires properties peculiar to unsaturated compounds

Some doubt must still exist as to the cause of the adherence to linkage in pairs in these circumstances, but it is clear that the attachment of a single hydrogen atom would disturb the balance of the rotating Benzenoid, while the attachment of two Hydrogen atoms in opposing or balancing positions would preserve the equilibrium of the molecule   This phenomenon may also be considered as due to the character of the Hydro-

gen atom   The Gas molecule of Hydrogen when it is
shaken apart to produce two atoms of nascent Hydrogen
may perhaps exist in a condition of partial separation,
so that the attachment of one atom involves the attach-
ment of the pair at the same time   Until further
knowledge is obtained and the form of the Hydrogen
atom is known, the solution of this problem must
remain in abeyance

CHAPTER VI

TAUTOMERISM

This phenomenon has received great attention from Organic Chemists and, under the title of "Dynamic Isomerism," has been the subject of a series of Reports to the British Association by a Committee presided over by Professor H E Armstrong

The subject has been dealt with at some length by Cohen[1] in *Organic Chemistry for Advanced Students*, from which the following extract is taken

"Since Laar drew attention to the subject in 1885, cases of tautomerism have rapidly multiplied Before discussing the later development of this subject, a short account will be given of a few of the principal types of tautomeric compounds, that is to say, compounds which possess a double function, but are commonly represented by only one substance

"If we examine the examples of tautomerism which have been given, we shall find that the structure of the compounds is such that it allows of the formation of isomers by the transference of a hydrogen atom from one polyvalent element to another, accompanied by a corresponding change in the

---

[1] Cohen—"*Organic Chemistry*," 2nd Edition, Part II Structure, p 318

linkages   This structure depends, therefore, on the
presence of certain groups

"A convenient plan of classifying the greater
number of tautomeric compounds has been pro-
posed by Laar, who divides them into 'Dyads'
consisting of two polyvalent elements linked to
gether, from one to the other of which the hydrogen
atom may be supposed to travel, '*Triads*' in
which the original two polyvalent elements are
separated by a third (which is of necessity at least
tervalent) so that the hydrogen has now to travel
from the first to the third element in the chain,
and so forth"

After quoting a large number of cases of tauto-
merism, Cohen sums up the subject as follows[1] —

"It will be seen that Laar's conception of one
substance representing two structural isomers has
not been consistently adhered to, for several cases
are cited in which both isomers anticipated by
theory are known   The latter have been called
Dynamic Isomers sometimes or desmotropic com-
pounds, to distinguish them from the single or
tautomeric substance   Dynamic Isomers differ in
no respect from ordinary Isomers but in the fact that
they are more or less readily inter-convertible   "

"Fresh light has been thrown on the subject
of tautomerism by the discovery of both structural
forms of the familiar and peculiarly labile (Keto-enol)
type of tautomeric compounds

[1] Cohen—"*Organic Chemistry*," 2nd Edition, Part II
Structure, p 330

"Its immediate result has been to demonstrate
the futility of the method hitherto adopted of
attempting to ascertain the structural formula of a
tautomeric compound from that of its derivatives
or from the chemical behaviour of the compound
itself

"It has been shewn that the extreme mobility
of one or both of the isomers renders them liable
to isomeric change only in presence of a reagent,
but frequently by a rise of temperature or the
mere action of a solvent "

The Committee of the British Association referred
to above in their Report state that Dynamic Isomerism
includes all cases of reversible isomeric change and
that it requires the aid of a catalyst to bring about
the reaction This is supplied by water or dust, and
that the change is not an intramolecular one, but is the
result of a complex heterogeneous molecular circuit [1]

Without entering upon a discussion of any of the
problems connected with this subject, we submit that
when viewed from the standpoint of the theory of Atomic
Form, cases of reversible Isomeric Change may be divided
into three groups, namely —

    (1) CARBON CHAINS
           Transfers from Carbon to an adjacent
           Carbon or to an atom or group attached
           to an adjacent carbon atom

    (2) THE BENZENE NUCLEUS
           Transfers from attachment to one part of
           the Ring to another part, or to a group
           attached to some other part of the Ring

[1] Report of the British Association (1909), p 137

(3) Triads

Transfers involving the passage of the labile Hydrogen from No 1 to No 3 η_1 the carbon framework passing over No 2

In all these cases we deal only with transfers of position in which carbon, oxygen and hydrogen are concerned Our ignorance of the probable form of Nitrogen and other elements renders it inadvisable to include transfers in which these atoms are involved

(1) CARBON CHAINS

In the well-known example of aceto-acetic Ester, the two interchangeable forms are

$$CH_3{-}COH{-}CH{-}COO{-}C_2H_5$$

and

$$CH_3{-}CO{-}CH_2{-}COO{-}C_2H_5$$
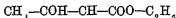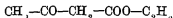
the labile Hydrogen may be represented as oscillating between the two positions, thus —

$$\begin{array}{cccc} & H & H & O \\ & | & | & | \diagup \\ H{-}C{-}C{-}C{-}C{-}C_2H_5 \\ & | & | & \diagdown \\ & H & O \diagup H & O \\ & (1) & (2) & (3) \quad (4) \end{array}$$
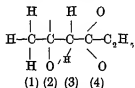
In a chain of four carbonoids there exist three co-basal pairs of faces, Nos 1—2, 2—3, 3—4 In the pair 2—3, No 2 carries an additional Oxygen Atom and the distance between a face of the Oxygen Atom and a face of No 3 Carbon is quite small It is not surprising if the attraction of the Oxygen attached to No 2 is balanced by the attraction of Carbon No 3, and in such a condition the Hydrogen might have a tendency to oscillate between the two positions

Assuming for Oxygen an imaginary form of a tri-angular Prism, with two faces equal to a face of the car-bonoid, the position will be represented by one of the following drawings —
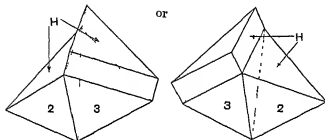
Fig 32

One cannot suppose that the very light atom of Hydrogen is tightly held by the attraction of the car-bonoid, and when the temperature of the system is raised and the rotation of the molecules increased, the Hydrogen will momentarily leave its position in the molecule, and on returning will, in some cases, attach itself to the Oxygen

Such an interchange seems very probable, even on the assumption of spheres or cubes for the forms of carbon and oxygen, thus —
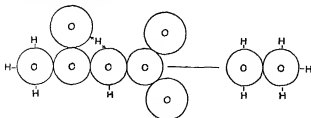
Fig 33

(2)   THE BENZENE NUCLEUS

An example of this type of tautomerism is given by
Professor Cohen

NITROSO PHENOL   QUINONE-OXIME

These formulæ represent the distance over which
the Hydrogen atom travels to be the entire diameter of
the Benzene Ring   On looking at the Benzenoid it is
seen, however, that this is a comparatively short dis-
tance   See Fig 34
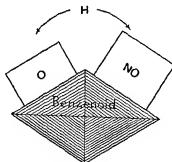
Fig 34

The Oxygen and the Nitroso group will be in close proximity near the centre of the Benzene nucleus, and there is a strong probability of a Hydrogen atom being attracted from one to the other

(3)   TRIADS

Examples of this type are numerous and include transfers from carbon to carbon and between the elements Carbon, Nitrogen and Oxygen   What the relative positions of the two atoms between which the Hydrogen is presumed to oscillate may be, we cannot tell, except where we have three carbons as in the following type

$$R\text{——}\overset{(1)}{C}\text{——}\overset{(2)}{C}\text{——}\overset{(3)}{C}\text{——}R$$
$$\overset{\frown}{\text{H}}$$
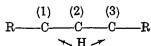
There are three ways in which three carbonoids may be arranged, viz —

The right handed form, ⎫ either of these is repre-
The left handed form, ⎬ sented by Figs 44 and
The straight form,   ⎭ 45, p 72a

In the first two of these forms there is a concavity separating one of the faces of No 1 from one of the faces of No 3, and a transfer of Hydrogen from one of these faces to the opposing face or to a group occupying the opposing face and *vice versa* could most easily be made See Fig 35, p 56

It will be seen that the intervening carbon, No 2, occupies a position which entirely removes it from the field of action
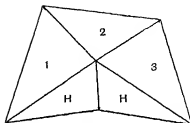
Fig 35

In the case of an Oxygen atom occupying one of the faces of the concavity, the transfer of the Hydrogen atom becomes facilitated

It is claimed that the existence of Tautomers of this type is a strong confirmation of the theory of Atomic Form, as only in chains of three or more tetrahedra, can an arrangement be made of such a type that the first and third of the tetrahedra are in close proximity and so readily suggest oscillation of the Hydrogen atom between the opposing faces

This result may be achieved either intramolecularly or by a complex molecular circuit, for if the Hydrogen is entirely removed from the molecule to form part of a molecule of water or of some other chemical aggregate, and is then returned to the original molecule containing three carbon atoms, it would have the same opportunity of becoming attached to either side of the concavity

Lapworth, in a paper on a possible basis of generalisation of Intramolecular Changes in Organic Compounds, states that the majority of reactions and changes

in Organic Chemistry, can be referred to necessary varia-
tions of one, or at most, two, simple laws, which find
their most general forms in the relationship between,
for example, the two forms of tautomeric and desmo-
tropic substances, as for instance $R_a M_1$ R_β $R_\gamma M_2$
$\rightleftarrows$ R_a R_β $R_\gamma M_1 M_1$, $\rightleftarrows$ $R_a M_2$ R_β $R_\gamma M_1$, and
he suggests the following graphic representation to
explain the transfer of M from No 1 to No 3
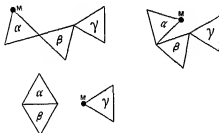
In this connection he suggests that it is not necessary
to imagine that the group M ever actually becomes free,
but rather that it is always under the influence of the
attraction of R_a or R_γ, and possibly at some instant
of both simultaneously, thus the labile character of the
molecule may be imagined to depend upon a species of
dissociation [1]

The graphic illustration shewn in the paper, of which
a copy appears above, is evidently designed to shew
how a labile atom may be transferred from No 1 to No
3 passing over No 2   Transfers of this character are
clearly provided for in all carbonoid groups, as already
explained, see Fig 35

[1] Journal of the Chemical Society, Vol 73, p 445, (1898)

E

CHAPTER VII.

ISOPRENE AND RUBBER

The models may be used as a means of deciding which of two formulæ is to be considered as the correct one   As an instance, let us take the model of Isoprene, Fig 36, p 58a

$$
\begin{array}{c}
\qquad\qquad\qquad \backslash \\
\qquad\qquad\qquad CH_3 \\
| \qquad\quad | \qquad /\,(4) \\
CH_2\!-\!CH\!-\!C \\
(1) \quad (2) \quad (3)\!\!\!\searrow \\
\qquad\qquad\qquad CH_3 \\
\qquad\qquad\qquad (5)
\end{array}
$$
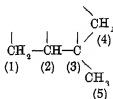
At the Meeting of the British Association at York in 1906, W A Tilden reported on the polymerization of Isoprene, he then stated :—[1]

> " It appears probable that the slow polymerization which ultimately results in the production of solid India-rubber is due to a different mode of linkage, leading to the formation of long chains   Except on the assumption of a shifting of Hydrogen this can only take place on the condition of the formation of a series of tetramethylene rings "

[1] Brit Assoc Reports, York, (1906), p 525
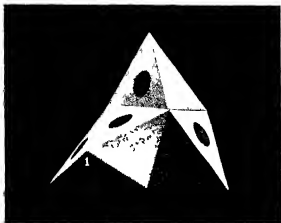
Fig 36
Model of Isoprene
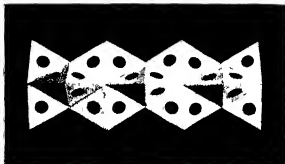
Fig 37
Chain of Carbon Atoms of indefinite length

NOTE —The black spots indicate the positions assumed to
be occupied by Hydrogen

If a change takes place gradually in the position of the " H " atom so as to produce the following —

```
              H   H
               \ /
                C—
        |    H  \ /(4)
  H — C — C — C  \
     (1)| (2)|  (3) \
        H   H        C—
                   / |(5)
                  H  H
```
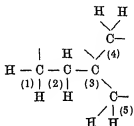
the molecule will be of such a form that two pairs of co-planar faces would be presented, viz   Nos 1 and 3 and Nos 4 and 5, and these would be available for linking to another molecule of Isoprene

By reason of these two pairs of co planar faces (see the annexed photograph, Fig 36), molecules of this kind could form long chains or filaments of indefinite length, which would be marvellously fine and delicate, but as the carbon atoms will be held together by their mutual attractions only, they would always be capable of a slight separation at each joint in the carbon chain, the existence of an enormous number of such joints in a small piece of each filament would produce a power of stretching and recovery of a marked character

The appearance of the chain of carbon atoms is shown in the photograph Fig 37, and may be extended indefinitely

Harries has put forward an eight membered ring formula
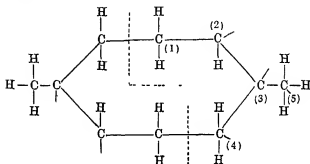
The carbon No 4 in the formula of Isoprene

$$\begin{array}{c} | \\ CH_2 \\ | \quad\quad | \quad |\;\diagup(4) \\ CH_2\!-\!CH\!-\!C \\ (1)\quad(2)\quad(3)\diagdown \\ \quad\quad\quad\quad CH_3 \\ \quad\quad\quad\quad(5) \end{array}$$
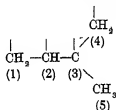
is assumed to form part of the eight membered ring, but our models shew that the three carbons (4), (3) and (5) form part of an independent ring

They also shew that the unoccupied faces or unsaturated linkages of the CH_2 (1), CH (2) and C (3) are also part of another ring and that CH_2 (1) and C (3) form a co planar pair of faces, C (3) being common to both rings, and that on the removal of one Hydrogen from CH_2 and the transference thereof to CH making it
          (5)   (2)

CH_2, the two atoms CH_2 and CH_2 form another co-
  ɔ   (4)   (5)
planar face, both of which are available for linking to
another similar molecule

It will thus be seen that before Isoprene can poly
merize a change in the arrangement of the Hydrogen
is necessary   One of the Hydrogen atoms in CH_2 being
                                                    (5)
removed to the unoccupied linkage of CH
                                     (2)

In the above formula this appears to be a difficult
operation, as the Hydrogen would have to pass over C,
                                                    (3)
but when the models are inspected, it is seen that these
atoms are adjacent, see Fig No 36, p 58a, where the
relative positions of No 2 and No 5 are shewn   It will
thus be apparent that the shifting of Hydrogen men-
tioned by Prof Tilden in 1906 can now be shewn to be
a probable occurrence

Although CH_2 and CH are now shown to be adja
             (5)   (2)
cent atoms, the two faces concerned in the necessary
transfer of Hydrogen are not *adjoining faces*, and it
appears to be necessary to pass over to the other side of
CH_2 in order to reach CH   This is not a difficult
 (5)   (2)
transfer, but it is probable that it will not take place
immediately nor very readily , this may be considered
to be consistent with the slow rate at which poly-
merization of Isoprene takes place

It seems highly probable that gradually the juxta-position of another molecule with a co-planar face, free from Hydrogen, will cause the removal of a Hydrogen atom from the CH_2 group and its transference to CH

$$(5) \qquad\qquad (2)$$

When this change takes place, the polymerization of Isoprene will immediately follow, and if this be continued the long delicate filaments of caoutchouc will result   These filaments will not crystallize, but lying in close contact extending in all directions would constitute a highly elastic solid, provided we may assume that the property of elasticity possessed by India-rubber is due to the stretching and recoil of these filaments

Pickles, in a paper read before the Chemical Society of London in 1910[1], suggested that the unsaturated nuclei C_5H_8 of Isoprene might unite to form long chains of the following structure

$$\begin{array}{ccccc} Me & & Me & & Me \\ | & & | & & | \\ CH_2\ C\ CH\ (CH_2)_2 & C & CH\ (CH_2)_2\ C & CH\ (CH_2)_2 \end{array}$$
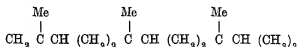
and that the number of C_5H_8 complexes involved in the chain might vary in different kinds of Rubber   His formula for Isoprene is

$$\begin{array}{c} | \quad | \quad | \quad | \\ H-C-C-C-C-H \\ | \quad | \quad | \quad | \\ H \quad | \quad H\ H \\ H-C-H \\ | \\ H \end{array}$$
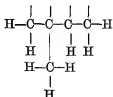
and he shews grounds for rejecting the eight membered ring proposed by Harries

Models can be prepared in accordance with Pickles' formula, but they are not of a compact or symmetrical form, and the chains would be of two kinds, right and left handed and involving optical activity (see Chapter IX) We think that the carbonoid chain shewn in Fig 37, p 58a, is the most probable explanation of the structure of rubber, although it involves a change in the position of one Hydrogen atom

In Stewart's *Recent Advances in Organic Chemistry*,[1] the subject of Natural and Artificial Rubber and the various syntheses of the artificial product are fully considered, and it appears that normal rubber can be prepared from Isoprene, by the formation of an intermediate product called $C_{10}H_{16}$, resulting from keeping Isoprene at a temperature of $80°—90°$ This dimeric form is subsequently treated with Sodium for the production of Normal Rubber

From what has been already stated with regard to the model of Isoprene it will be seen that each molecule has one co-planar face, (Nos 1 and 3 in the above formula), available for linkage to another molecule of Isoprene without any change in the arrangement of the attached Hydrogen, so that when the substance is submitted to a moderate temperature the β Myrcene compound is formed

The further polymerization requires the assistance of Sodium, and a change in the position of one of the Hydrogen atoms as above explained

[1] Stewart—" *Recent Advances in Organic Chemistry*," (1920), p 103 116

Even if the reader is unable to accept the Scheme
of Atomic Form he will find that the use of models
will in this case assist him in the consideration of the
formulæ, and by shewing the existence of pairs of
co-planar faces (Nos 1—3 and Nos 4—5) will enable
the formation of a filament to be more easily appre-
hended

CHAPTER VIII

TRIPHENYL-METHANE

$(C_6H_5)_3$ CH or $C_{19}H_{16}$
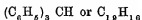
Some attention should be given to this compound on account of its theoretical importance The group $(C_6H_5)_3$, or $(C_6H_4)_3$, combine with Nitrogen and other groups, occupies an unique position in the molecule of many important Chemical Dyes, including the rosanilines It also polymerizes to form Hexaphenyl-ethane $(C_6H_5)_3$, C—C $(C_6H_5)_3$

Consideration of the models indicates that while it may be possible to arrange three Benzenoids around a single Carbonoid, the arrangement is not symmetrical and the resulting model of the Triphenyl methane molecule is not at all likely to be stable

The arrangement of three Benzenoids around one Carbonoid is suggested by the formula, the idea evidently being that one Hydrogen must be omitted from each Benzene Ring, so as to allow of a linkage to the single carbon which is supposed to be situated in the centre of the molecule, the remaining affinity being represented by the single Hydrogen attached to the central carbon The compound was thus made to appear to be saturated, except for the normal unsaturation of the Benzene Rings

For a long time, it appeared that this was one of the most difficult cases, arising in connection with the

Theory of Atomic Form   Further consideration, how-
ever, shews that the method of arrangement shewn in
Fig 38 may be adopted

In the synthesis of Triphenyl-methane, Benzene
takes an important part, as shewn below

$$(C_6H_5) \begin{array}{c} H \\ | \\ C \\ | \\ O \end{array} +2(C_6H_6)=(C_6H_5)_3CH+H_2O$$

$$(C_6H_5)CH-Cl_2+2(C_6H_6)=(C_6H_5)_3CH+2HCl$$

$$CHCl_3+3(C_6H_6)=(C_6H_5)_3CH+3HCl$$
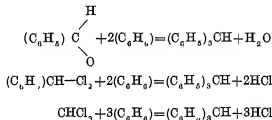
It is true that the Hydrogen may be supposed to
retain its place in attachment to the single carbon and
that each of the Benzene Rings may give up one Hydro-
gen, but it may equally well be the case that
only one Hydrogen is taken from Benzene and one
from the attached Carbonoid, or that the single
carbon takes on an additional Hydrogen, making
CH_2 leaving one of the Benzene Rings with only
four, but it seems reasonable to adopt the scheme
by which the extra Carbonoid is attached to
the Triphenyl group, and does not constitute the
centre of the molecule   It is introduced into the mole-
cule in attachment to one Benzene Ring, and the mole-
cule is completed by the association of two additional
Rings   In doing so they may each give up one Hydro-
gen in order to complete the molecule of Water or
Hydrochloric Acid, without becoming directly attached
to the single Carbon
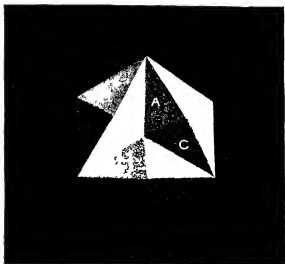
Fig 38
Tri phlnyi Methane
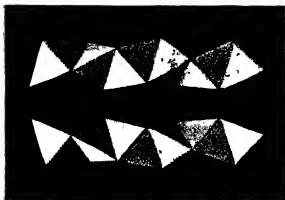
Fig 43 (See p 74)
Right and left handed Spirals
Asymmetric arrangement of the Carbonoid Chain

It must be remembered that the Phenyl group has one side entirely unsaturated and therefore available for attachment to other Rings Three Benzenoids have therefore three sides which can be brought into contact free from any hindrance caused by attached Hydrogen The unsaturated sides of the Benzenoid have each two faces which can be arranged so as to form attachments to other Benzenoids

The form of the Benzenoid is such that a new complex is thus formed of a compact and stable configuration, a photograph of which is shewn in Fig 38

To a molecule of this configuration a carbon atom may be attached in such a way as to produce a co-basal and co planar pair of faces, available for union with any other molecule of Triphenyl methane or with other groups

In order to express the arrangement of the carbonoids in this molecule a special type of notation will be used viz

BENZENOID
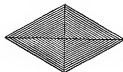
Fig 40

View from the side of the molecule

The Tri phenyl Group $(C_6H_5)_3$ will be indicated thus —

C_{18}
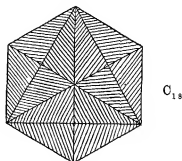
Fig 41

The Hydrogen may be arranged in three different ways —

I   II   III

C_6H_5 C_6H_5 C_6H_6 C_6H_5 C_6H_4 C_6H_5

C_6H_5 C_6H_5 C_6H_5

CH   C CH_2
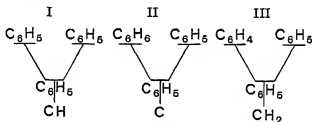
In all three of these arrangements there will be four unsaturated faces distributed between the C_6H_5 groups and the single carbonoid   In each arrangement there will be a co-planar face between C_6H_5 and CH or CH_2, respectively, and in No III there will be, in addition, two single unsaturated faces on the opposite side of the molecule (C_6H_4) and in No 1, one such face   The

unsaturated condition of the group corresponds to the molecule's remarkable power of forming addition products with ether and many other compounds and the readiness with which oxidation takes place

A complete double molecule of Triphenyl-methane will be represented thus —

$$(C_{19}H_{16})_2$$
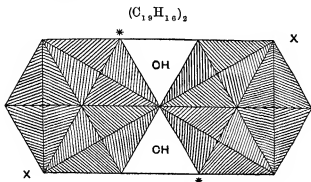
Fig 42

The co planar faces extend from * to *
The unsaturated faces are situated at *

It will be seen that the double molecule is capable of further attachment to other atoms or groups The model shews that for each *single* molecule there is one unsaturated face on the opposite side of the phenyl group as well as a coplanar face, and a vacant face on the back of the methyl group CH If the methyl has two Hydrogen in attachment, there will be two faces vacant on the opposite side of the Tri-phenyl group, and this might enable a net work to be built up which could be extended horizontally in all directions

The double molecule above depicted corresponds to Hexaphenyl ethane, the carbon linking in which can be so easily broken , this is easily understood when the masses of the two triphenyl groups are considered and the fact that they are not directly linked together

$$\text{In rosaniline} \quad HO-C \begin{array}{c} C_6H_4NH_2 \\ \diagup \\ -C_6H_4NH_2 \\ \diagdown \\ C_6H_4NH_2 \end{array}$$
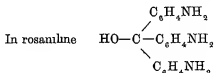
three amino groups are attached to the three phenyl groups and one hydroxyl group is attached to the additional carbon, but leaving the triphenyl group unaltered and leaving four unsaturated faces including the co-planar face already mentioned

In rosaniline and other compounds containing amino groups, Oxygen, etc , the construction of a crystalline form is probably assisted by the attached groups and atoms

The Triphenyl group is capable of carrying six atoms attached to the two opposing sides of two phenyl groups in the positions marked AA, BB and CC above and below in the foregoing illustration, Fig 38, p 66a These faces, however, do not appear to be occupied There would probably be difficulty in introducing a Carbonoid into these positions

Although the theory of the constitution of Triphenyl-methane set forth above has some points in its favour, it is not free from difficulties It is maintained by some chemists that Triphenyl methane should be considered

as a methyl group, surrounded by three phenyl groups, all three being in contact with the central carbon This view is supported by the fact that it can be synthesized from Benzene and chloroform and that one of the Hydrogen atoms, being in union with the central carbon, acts differently from all the others and on oxidation becomes reduced to —OH

It must also be acknowledged that the Chemical evidence with regard to Triphenyl-methane points to the methyl group being an essential part of the molecule without which it could not exist In the position which we have assigned to it in attachment to the out side of the Triphenyl group it could be dispensed with, leaving a group which we should expect to be able to isolate and to record its characteristics

The constitution of Triphenyl methane has been the subject of much speculation and controversy, and doubts exist as to whether the molecule is not a double one in the form of Hexaphenyl ethane, although readily decomposed into Triphenyl-methyl in which form it recombines with other atoms and groups

If this view is correct, the difficulties surrounding the constitution of the molecule would to a large extent disappear, since in Hexaphenyl-ethane the two carbon atoms are shewn to be in the centre of the group

Whatever form is assigned to Carbon it is difficult to conceive of three Benzene rings (77 each), attracted and held by a single carbon atom in the centre of the molecule

It is clear that the question of the constitution of Triphenyl-methane and Hexaphenyl-ethane is open to considerable doubt and must be reserved for further consideration   This subject is fully discussed in Stewart's " *Recent Advances in Organic Chemistry*," Chapter IX [1]   In the 5th section of this chapter he writes —

> " We have now exhausted the possibilities of static formulæ to explain the behaviour of Tri-phenyl-methyl , and it is evident that the results have not been completely satisfactory   All the three views which we have discussed in the foregoing sections have certain advantages , and each has its own drawbacks   It thus becomes clear that, if we are to make any further progress towards a solution of the problem, we must contrive some means of uniting the advantages of the various formulæ , while at the same time we must endeavour to minimise their weak points   In order to do this it is obvious that we must turn to modern dynamic ideas and represent Triphenyl-methyl as a series of equilibrium mixtures of isomerides   Gomberg has developed this line of thought   and if his results do not represent the truth, it seems probable that they come very close to it "

It is hoped that the suggestions put forward in this chapter may be of use in helping towards the solution of a problem of much complexity and difficulty

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[1] *Stewart*—" *Recent Advances in Organic Chemistry*," (1920), p 295
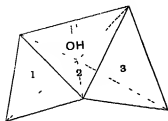
Fig 44a
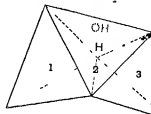
Fig 44b
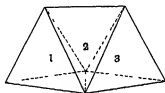
Fig 45
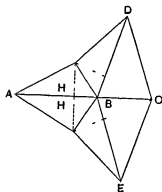
Fig 50

a   b

Fig 46 OPTICAL ISOMERS

a   b

Fig 47 OPTICAL ISOMERS

Fig 48 INACTIVE FORMS Fig 49

CHAPTER IX.

OPTICAL ACTIVITY OF CARBON COMPOUNDS

In the year 1860, PASTEUR, by his researches on the Tartaric Acids, laid the foundation of Stereo chemistry, and Van't Hoff[1] in 1898, quoted the following instructive passage from PASTEUR's writings —

> " Are the atoms of Tartaric Acid arranged along the spiral of a right-handed screw, or are they situated at the corners of an irregular tetrahedron, or have they some other asymmetric grouping? Time must answer the question   But of this there is no doubt, that the atoms possess an asymmetric arrangement like that of an object and its mirrored image   Equally certain is it that the atoms of the left handed acid possess just the opposite asymmetric arrangement "

During the sixty years that have passed since these words were written, an enormous amount of study has been given to asymmetric Isomerism, and a mass of detail has been recorded ; the subject is still, however, involved in much controversy and speculation, and many problems await solution

[1] *The Arrangement of Atoms in Space,* 2nd Edition, p 12, (1898), J H Van't Hoff

F

Stewart, in *Stereochemistry*,[1] writes —

"In the purely stereochemical field, much yet remains to be done in the examination of isomeric compounds for the existence of which no explanation can be adduced under current theories"

It is claimed for the theory of Atomic Form that right handed and left handed spirals are displayed by the carbonoid when arranged to represent carbon chains, resulting in an asymmetric arrangement like that of an object and its mirrored image The two spirals are shewn in Fig 43, p 66a

The Carbonoid itself is an *irregular* Tetrahedron, as suggested by Pasteur, and to its special configuration is due the asymmetry of the carbonoid chain and its power of depicting a large number of carbon compounds

With the view of simplifying the discussion of the optical activity of carbon, it is proposed to omit all reference to stereoisomerism arising in compounds of other elements, such as Nitrogen, Silicon, Tin, Cobalt, etc

While on one hand the current theories do not afford a satisfactory explanation of many facts connected with this branch of chemistry, the Theory of Atomic Form has no magic wand by which it can explain the complex problems involved It is proposed to set out certain features of the theory bearing upon the subject and to await the extension of our knowledge and the result of further experimental research

---

[1] Stewart—"*Stereochemistry*," 2nd Edition, (1919), p 240

The Carbonoid Aggregates for two carbonoids only
exist in one form, the " Ethyloid," but on proceeding to
arrange *three* carbonoids there are three different forms
available called " Tricarbonoids," drawings of which are
shewn in Figures 44a and b, and Fig 45, p 72a The
two Figs 44a and 44b are mirror images of one another
and cannot be superimposed   They are the beginnings
of the two spiral chains, the forms assumed by strings
of carbonoids—such chains are in two forms, the spiral
figure being directed round the chain in the form of a
right-handed screw in one case and as a left-handed
screw in the other, as will be clearly seen by the photo
graph of two chains of 17 carbonoids each, Fig 43, p 66a

It is interesting to note that no compounds shew-
ing optical activity have less than *three* carbon atoms
in the molecule, with the exception of

<div align="center">Chloro-iodo methane sulphonic Acid</div>

$$\text{(a)}-\text{H}-\overset{\displaystyle \text{Cl}}{\underset{\displaystyle \text{I}}{\text{C}}}-\text{SO}_3\text{H}-\text{(b)}$$
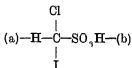
<div align="center">and Fluoro-chloro-bromo acetic Acid</div>

$$\text{(a)}-\text{Cl}-\overset{\displaystyle \text{F}}{\underset{\displaystyle \text{Br}}{\text{C}}}-\text{COOH}-\text{(b)}$$
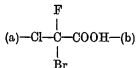
Both of which have been resolved into two optical
isomers [1]

[1] Stewart—" *Stereochemistry,*" 2nd Edition, (1919), p 11

In the first case, if the central carbon is represented
by a Sphere, it would be difficult to arrange the atoms
so as to represent two right and left-handed Isomers,
as the figure could be rotated around the axis $a—b$
without altering its appearance, and any change in the
relative positions of the Chlorine and Iodine atoms would
be nullified by revolving the molecule in this way, the
same would apply to the second case   If however the
central carbon has a tetrahedral form, it will be possible
to exchange the positions of the Chlorine and Iodine in
the first case, and the Fluorine and Bromine in the second
case, thus producing in each case two isomers which
will be mirror images of one another, and enantiomorph
ism will result

Compounds of this type appear to belong to a
different class from the optically active compounds of
3, 4 and 5 carbons which we are now considering

It may therefore be stated that the Theory of
Atomic Form agrees generally with the facts, in regard
to the point at which the optical activity of carbon
compounds commences

A large number of Optical Isomers are known
where it is clear that the isomerism is due to the trans-
position of an atom or group from one side to the other
of the molecule, even in some cases where no asymmetric
carbon atom is disclosed, such a compound is 1 methyl-
cyclo-hexylidene 4-acetic acid

$$(b)\ CH_3\quad CH_2—CH_2\qquad\qquad H\ (c)$$
$$\diagdown\qquad\diagup\qquad\qquad\diagup$$
$$C\qquad\qquad C—C$$
$$\diagup\qquad\diagdown\qquad\qquad (4)\ (7)\diagdown$$
$$(a)\quad H\qquad CH_2—CH_2\qquad CO_2H\ (d)$$
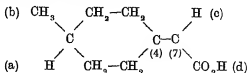
This substance is discussed in a paper read before Section B of the British Association at Portsmouth (1911), by Wm H Perkin and Wm Jackson Pope [1]

The synthesis was described and the substance resolved into its right- and left-handed isomers

The writers of the paper decided that the groups marked (a) and (b) do not lie in the plane of the paper, but in a plane at right angles to the six carbon atoms forming the ring Similarly the two carbons at the other end of the ring marked (4) and (7) are in the same plane as groups (a) and (b) but the two groups (c) and (d) are again in the same plane as the paper

If a model is made of this molecule, using carbonoids to represent the carbon atoms, the form presented will shew all the features described above, and the right-and left-handed configurations due to the positions occupied by the groups (c) and (d) relatively to the rest of the molecule will be made evident If the positions of H(c) and CO_2H(d) are interchanged, we get the mirror image of the original figure and the two optical isomers are produced

The authors of the paper have described this con-figuration as " centro asymmetric " They state that compounds of this type open up a wide field of enquiry

It is submitted that—whatever view may be held with regard to the Theory of Atomic Form—it will be found that the use of models of carbonoids will facilitate the study of these more complicated compounds, and enable the position in the molecule of the various groups to be more readily understood

[1] But Assoc Reports, Portsmouth, (1911), p 361

A simpler case is that of secondary Butyl carbinol

$$
\begin{array}{ccc}
\text{H} & \text{H} & \text{H} \\
| & | & | \\
\text{H—C——C——C—OH} \\
\text{(2)} \; | & | & | \; \text{(1)} \\
\text{H} & | & \text{H} \\
& \text{H—C—H} \\
& | \\
& \text{H—C—H} \\
& | \\
& \text{H}
\end{array}
$$
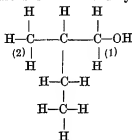
Here the groups marked (1) and (2) may be assumed to change places, and as the form of the chain of carbonoids is such that it presents an entirely different aspect when viewed from the other side, the result of such a change of position would be to produce two isomers which would be related to one another, as an object is to its mirrored image   It is possible that the two carbons may not be disturbed, the same effect being produced by the interchange of Hydroxyl and Hydrogen

Many other examples of Isomerism of this type might be quoted, in which it is unnecessary to assume any spiral formation of the chain of carbonoids—the optical activity being due to a change in the position of the attached groups, without any alteration of the relative positions of the carbon atoms

There remain, however, certain compounds of a different class in which there is considerable difficulty in ascribing the existing Isomerism entirely to a change in position of Hydrogen, Hydroxyl, or other groups in the molecule, and where it seems reasonable to suppose that the spiral form of the chain of carbons is involved

We now turn to the consideration of some of the typical cases of compounds of this class containing four carbon atoms

There are seven different arrangements of four carbonoids possible, as shewn in Figs 46a and b, 47a and b, 48, 49 and 50, pp 72a and b If an additional carbonoid be added to one of the two groups of three carbonoids shewn in Figs 44a and b, p 72a, six new figures are produced, viz Nos 46a and b, 47a and b, 49 and 50 In Fig 46a and b the spiral chain is continued in the two mirror image forms, and in Fig 47a and b two isomeric forms are produced of opposite configuration, but in Figs 49 and 50 the enantiomorphous configuration disappears, and these Figures may be derived from either 44a or 44b, with the same result

In the same way, the addition of a single carbonoid to either of Figs 44a or 44b, if attached to either of the sides of the concave pair of faces of either a or b forms, will produce Fig 49, in which again the spiral configuration has disappeared

A single carbonoid can be added to Fig 45, p 72a in four ways if it be attached to one of the end carbon oids two figures are produced either 47a or 47b, which are mirror images of one another, if attached to the middle carbonoid on either side Fig 50 will be produced Fig 48 is produced by adding one carbonoid to the base of No 45 on either side

All the seven forms of four carbonoids can be produced by different arrangements of Ethyloids except Fig 50

In the present state of our information regarding chemical transformations, there appears to be nothing to be gained by attempting to trace a correspondence between the changes of form effected by the addition of one carbonoid, as above stated, and the differences in form of compounds of three or four carbons The compounds containing four carbons are mostly derived from the analysis of coal tar or from natural products, such as the acids of grapes and other fruits The single carbon atom is not usually available, except in the saturated condition, and when changed to a nascent state by the loss of Hydrogen, it immediately forms a compound containing two or more carbons in the molecule

But in whatever way the compounds of four carbons are formed, the carbonoid furnishes us with seven different configurations, some of which may have no counterparts in any compounds at present known, but others can fairly be assigned to well-known substances

In order to limit the scope of this enquiry, we propose to consider certain typical cases of compounds containing four carbons only, viz —

—A— —B—

1. *d*— and *l*— Malic Acid   Crassulaic Malic Acid

$$
\begin{array}{c}
\text{HO } \text{ H} \\
| \quad | \\
\text{HOOC—C—C—COOH} \\
| \quad | \\
\text{H} \quad \text{H}
\end{array}
$$

—A—   —B—
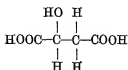
2 *d*-and —*l* Tartaric Acid   Mesotartaric Acid

$$\begin{array}{c} \text{OH H} \\ |\ \ | \\ \text{HOOC—C—C—COOH} \\ |\ \ | \\ \text{H   OH} \end{array}$$
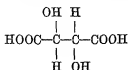
3 Fumaric Acid   Maleic Acid

$$\begin{array}{c} \text{H H} \\ |\ \ | \\ \text{HOOC—C—C—COOH} \\ |\ \ | \end{array}$$
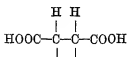
4 Crotonic Acid   Isocrotonic Acid

$$\begin{array}{c} \text{H H H} \\ |\ \ |\ \ | \\ \text{H—C—C—C—COOH} \\ |\ \ |\ \ | \\ \text{H} \end{array}$$
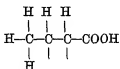
Each of the above four groups exhibits an Isomerism with well marked differences between the Isomers, A and B, affecting both their chemical and physical characteristics, including melting point, etc , and in addition, Nos 1 and 2 shew also another kind of Isomerism in which the two isomers while agreeing in nearly all their characteristics, are distinguished by the power of deflecting the beam of polarised light—by one isomer to the right and by the other to the left

Although there are difficulties to be met by any theory which seeks to explain this isomerism it is proposed to submit the suggestion that the carbon framework of all these compounds differs in its configuration,

$e\,g$, dextro Malic Acid differs from lævo Malic Acid
and these two again differ from Crassulaic Malic Acid,
these differences being due to the arrangement of the
carbon atoms within the molecule, which can be re-
presented by differences in the arrangement of the four
carbonoids

The Carbon framework of the compounds appearing
in Col " B " above may be represented by one or more of
Figs 48, 49 or 50, pp 72a and b, and the optically active
isomers in Col " A," Malic Acid and Tartaric Acid may
be represented by the right- and left handed forms shewn
under Figs 46a and b, or 47a and b   If this question
is accepted the opposite and equal optical activity of
the two isomers will be satisfactorily explained, without
having recourse to any assumptions with regard to
the positions of the attached atoms of Hydroxyl and
Hydrogen

At the present time the peculiar Isomerism with
which we have to deal, in the Malic and Tartaric Acids
is attributed to the position in the molecule of the
Hydroxyl or Hydrogen groups and to certain alleged
changes in the directions along which the mutual
attractions of the carbon atoms are supposed to operate

Van't Hoff and Le Bel have also expounded the
law that optical activity depends upon the presence in
the molecule of an asymmetric carbon atom, and al-
though some exceptions to this law have been dis
covered, it must be considered as holding good as a
general rule

The theory of Atomic Form attributes this right-
and left-handed Isomerism to alterations in the form
of the carbon framework, although it seems highly

probable that all such alterations are accompanied by changes in the positions occupied by the Hydroxyl and Hydrogen in attachment

It has been assumed that the two isomers which re present the dextro and lævo modifications are distin guishable from one another by a difference in the arrangement of the attached atoms or groups, and that a further change in the positions of these groups is the cause of the additional Isomer such as Crassulaic Malic Acid and Meso tartaric Acid   In Malic Acid, however, it is impossible to provide three different arrangements of the Hydroxyl group   In the formula

$$
\begin{array}{c}
\text{COOH} \\
| \\
\text{HO—C—H} \\
| \\
\text{H—C—H} \\
| \\
\text{COOH}
\end{array}
$$

if it be allowed to rotate the molecule in the plane of the paper, and also around its longer axis, no effective variation can be made   If however only one change of position is allowed, viz, a rotation in the plane of the paper, two different formulæ can be designed, viz —

$$
\begin{array}{cc}
\text{COOH} & \text{COOH} \\
| & | \\
\text{HO—C—H} \quad & \quad \text{H—C—OH} \\
| & | \\
\text{H—C—H} \quad & \quad \text{H—C—H} \\
| & | \\
\text{COOH} & \text{COOH}
\end{array}
$$

This leaves us without any further rearrangement possible—for Crassulaic Malic Acid—and even these formulæ are based upon the assumption of a difference in form between the back and front of the molecule, which is consistent with the view that the carbons have a definite geometric form, but which would not be appropriate, if the carbon is represented by a sphere —with equal attractions in four different directions in the plane of the paper—in which case, rotation around the longer axis would be possible   To meet this difficulty the following formulæ have been designed —

I	II	III
COOH	COOH	COOH
|	|	|
HO–C–H	HO–C–H	HO–C–H
|	|	|
HOOC–C–H	H–C–COOH	H–C–H
|	|	|
H	H	COOH
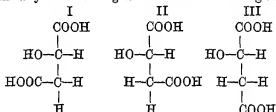
Formulæ I and II suggest that the Isomerism is due to a change in the position of the end carbons, and the formula is stated in such a way as to indicate a bend in the carbon chain to the right or left and in some measure accords with the theory of atomic form

Stewart, in "Stereochemistry," after setting out the "physical and chemical differences between common Malic Acid and Crassulaic Malic Acid," writes as follows —

"To account for this, it has been supposed that Malic Acid actually exists in three configurations (as shewn above), but this does not explain the effects which it produces upon the plane of polarisation   The question of the Isomerism is undecided at present

" Many other instances are known of isomerism
for which our current views offer no explanation,
and it seems advisable that further investigations in
these fields should be carried out, in order that
more facts may be accumulated "[1]

In explanation of the three formulæ on the preceding
page, it is represented that they are projections of the
Tetrahedral Models of Van't Hoff —Malic Acid being
represented thus

I   II   III
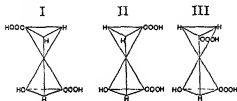
Here there are three possible arrangements, which
are alleged to represent the two d— and l— modifications
and Crassulaic Malic Acid

The question arises what meaning is to be attached
to these formulæ   Van't Hoff does not suggest
that the atoms of Carbon have a tetrahedral configura
tion   he states that the molecule is a "stable system of
material points,"[2] and he gives the extract from
Pasteur's writings, quoted on p 73   The Carbon atom
is represented as situated in the centre of a tetrahedron,
from which its four affinities or bonds are directed to
the four corners of the tetrahedron

---

[1] Stewart, " *Stereochemistry*," 2nd Edition, (1919), p 240
[2] " *The Arrangement of Atoms in Space*," Van't Hoff, 2nd
Edition p 5

Later investigators generally have not materially varied these conceptions, and modern Text Books contain statements based upon similar conceptions of the carbon atom

Cohen writes (1907)[1] —

"The internal motion of the atoms may be disregarded, and the centres about which they oscillate considered as a statical system of material points   How far the modern views of valency fit in with the idea of material points, whether the Valency of Carbon takes the form of a force acting in four directions, or of one evenly distributed over the atom , whether it is determined by a tetrahedral figure of the carbon atom or depends upon the sub-division of the atom into smaller parts, it is not our intention to discuss "

Stewart, in *Stereochemistry* (1919),[2] says —

"Many investigators have endeavoured to explain the origin of the tetrahedral grouping by assuming that the carbon atom is a material body of a certain shape and size   It is not necessary to deal with these views here "

A large number of references are, however, given to the writings of foreign chemists

[1] Cohen's " *Organic Chemistry*," (1907), p 67
[2] Stewart's " *Stereochemistry*," 2nd Edition, p 4

Any student who attempts to form a mental image of the structure of the molecule of Malic Acid is confronted with a difficult task,—he must imagine the carbon atom a system of *material points*, assumed to be held in its place in the molecule by forces acting through the points of a hypothetical tetrahedron, but which nevertheless must not be considered as being a body of any definite shape

The back-bone of the molecule of Malic Acid is clearly the chain of four carbon atoms, which appears in the Tartaric, Succinic and Crotonic Acids and in Fumaric and Maleic Acid, but these atoms are supposed to be united in the middle of the chain in such a way that rotation of the two upper carbons takes place around an axis passing through the *points* of two tetrahedra , no consideration being given to the method of union between the two carbon atoms forming the upper and lower halves of the molecule

In the place of these conceptions, the Theory of Atomic Form places before us a carbon atom of a certain shape, which naturally and inevitably combines to form two kinds of carbon chains, related to each other as object and image, the optical isomerism being considered as due to the configuration of the carbon chain, with or without any modification in the positions of the attached atoms or groups

It may be acknowledged that the tetrahedral conception which we owe to Van't Hoff and Le Bel has helped forward the study of optical Isomerides, but it is also true that a step forward is needed to enable clear and definite conceptions to prevail

We are therefoie unable to accept the above thiee formulæ (p 85) as a correct representation of the arrangement of the atoms in the two optical Isomers of Malic Acid, and in Crassulaic Malic Acid, which differs so markedly from them both

With iegard to the dextro and lævo forms of Tartaric Acid and Meso-tartaric Acid, the usual formulæ are as follows —

I	II	III
Dextro	Lævo	Meso
COOH	COOH	COOH
$\mid$	$\mid$	$\mid$
H–C–OH	HO–C–H	HO–C–H
$\mid$	$\mid$	$\mid$
HO–C–H	H–C–OH	HO–C–H
$\mid$	$\mid$	$\mid$
COOH	COOH	COOH
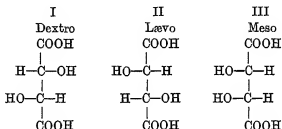
These formulæ are open to the objection already stated in connection with Malic Acid

There are considerable differences both chemical and physical between the ordinary Tartaric Acids and the Meso-tartaric type, while the differences between the dextro and lævo forms of the Acid are limited to the effect produced upon the ray of polarised light and the form of their crystals   It is submitted that, with such material differences as are shewn to exist between the ordinary Tartaric Acid and the Meso type, it is inconsistent to assign to the latter such a slight change in the arrangement of the constituent atoms as is shewn by the formula stated above , or if the large difference between the optically active and the Meso

Form is properly represented by the change in the position of one of the Hydroxyl groups—it is then inconsistent that the comparatively slight difference of character between the dextro and lævo modifications should also be represented by a similar change in the position of both Hydroxyl groups as shewn in the formula The isomerism of the dextro and lævo forms of Tartaric Acid is entirely different in character from that of Meso-tartaric Acid and calls for a well marked difference in the structure of the Meso as compared with the Racemic type

These difficulties are entirely removed if the modifications in the carbon chain shewn in Figs 46a and b, 47a and b and Figs 48, 49 and 50, pp 72a and b are adopted

On the other hand, it is at first sight somewhat difficult to assume that these modifications of the carbon chain can be made with the comparative ease which appears to be indicated in some of the reported reactions

By the Walden Inversion—lævo Malic Acid can be converted, by the action of PCl$_5$, into dextro-Chloro Succinic Acid, and this again by the action of AgOH into dextro-Malic Acid, thus effecting the change from the lævo form of Malic Acid into the dextro form—and this change is reversible If the theory of Atomic Form be adopted, this involves a change in the arrangement of the carbon framework from Fig 46a to 46b This does not seem so unlikely when the magnitude of the molecules taking part in the reaction is borne in mind —PCl$_5$ = 208, AgOH = 125 It seems fair to assume that the addition of a chlorine atom and its subsequent removal may be responsible for a rearrangement

G

of the carbon atoms in the molecule, the amount of
change in the carbon framework of the molecule being
comparatively slight as we shall shew presently

A greater difficulty arises however when we con
sider the statement that Malic Acid is laevo-rotatory
in dilute solutions but becomes dextro-rotatory when
the concentration is increased[1] Stewart adds

"In this case no change of configuration can
be assumed, and it is evident that configuration
and sign of rotation do not necessarily go hand in
hand"

Cohen,[2] commenting on this peculiarity of Malic
Acid, says

"The change of sign in the rotation of Malic
and Tartaric Acids   has been attributed to
the presence of molecular aggregates in the con-
centrated solution of opposite rotation, just as
crystal aggregates of a compound have been found
which differ in sign from their solutions   Imperfect
electrolytes, like the organic acids, exhibit in
solution a series of changes which depend generally
on the degree of dissociation

"The extent of dissociation is increased by
dilution and by rise of temperature, with a corres-
ponding numerical change in rotation"

It is scarcely possible on the strength of these
instances alone, to give up the view so long held, that
a change in optical rotation is associated with some
rearrangement of the atoms comprised in the molecule

---

[1] Stewart—"Stereochemistry," 2nd Edition, (1919), p 69
[2] Cohen—"Organic Chemistry," 2nd Edition, Part II
Structure, p 231

This view is strongly supported by the facts regarding the separate crystallisation of the dextro and lævo modifications and the right- and left handed forms of the crystals

The existence of this enantiomorphous configuration of the crystal, points to a difference in the method of arrangement of the molecules in the crystal, which is believed to be associated with a difference in the configuration of these molecules   If the molecular forms are identical and the change of sign of rotation is independent of configuration, it is difficult to see how two equal and opposite forms of the crystal can be obtained

If it be conceded that the molecule of an optically active isomer has a configuration which is the mirror image of the other isomer into which the compound is divisible, the question arises whether this form is due to the arrangement of attached groups, such as Hydroxyl or to an enantiomorphous configuration of the carbon framework of the molecule or to both causes together

A study of the models shewn in Fig 46, p 72b, shews that the two forms are so exactly alike in all respects, except that one has a right-handed and the other a left-handed configuration, and they appear to lend themselves so easily to the building up of two equal and opposite crystalline forms, that it is difficult to reject the view that in these models we have an explanation of the phenomenon of optical activity

The law of Van't Hoff and Le Bel and the persistency with which the presence of an asymmetric carbon atom in the molecule is associated with optical activity is partly explained by the following considerations

In the cases of carbon chains of 3, 4 and 5 carbons, nearly all the active compounds possess an Hydroxyl group, or some other atom or group of considerable size, the presence of which on one side of the chain and of a Hydrogen atom on the other side appears to be associated with optical activity, such an arrangement of the attached atoms and groups may probably be associated with the spiral character of the chain and of carbonoids, it naturally leads to the existence of an asymmetric carbon atom

As soon, however, as the Hydroxyl is removed, the optical activity disappears This is the case with Succinic Acid, Fumaric and Maleic Acids and the Crotonic Acids Succinic Acid is saturated with Hydrogen, but in the other Acids there is the difference between a Hydrogen linkage on one hand and an unsaturated condition on the other—a difference which might be expected to lead to optical activity in the Isomers, but none has been observed

It is suggested that as the presence of the Hydroxyl or other large group in the molecule renders the separation of the two Isomers possible, there are two conditions to be fulfilled in order that optical activity may be evident

(1) The compound must exist in two optical Isomers

(2) Means must exist whereby a separation of the two optical Isomers can be made

It is suggested that the presence of the Hydroxyl or other large group in the molecule renders the separation of the two Isomers possible, no separation taking place when the only difference is in the form of the carbon chain or a difference in arrangement of the attached Hydrogen

So long as no separation has been effected either during natural development or by artificial means, no optical activity can be discovered

CHANGES IN THE CARBON FRAMEWORK

It is clear that the form of the carbon framework must be subject to change in some circumstances, for instance, the following changes are recorded —

1 Malic Acid on heating produces both Fumaric and Maleic Acids, the particular Acid produced depending upon the temperature employed and the method of heating [1]

2 On oxidation, Fumaric Acid produces Tartaric Acid and Maleic Acid produces Mesotartaric Acid [2]

3 When acid is added to Sodium Thiosulphate in presence of Maleic Acid, Fumaric Acid is produced [3]

4 When Bromine acts upon Maleic Acid, Isodibromo-succinic Acid is formed [4]

5 When Bromine acts upon Fumaric Acid, Dibromo-succinic Acid (meso form) is produced

[1] Holleman—" Text Book of Organic Chemistry," Fifth Edition, p 211
[2] Holleman—" Text Book of Organic Chemistry," Fifth Edition, p 244
[3] Stewart—" Stereochemistry," 2nd Edition, p 122
[4] Stewart—" Stereochemistry," 2nd Edition, p 116

6   Both Fumaric and Maleic Acids yield Succinic
Acid on treatment with Sodium Amalgam and
Water, and both Acids may be transformed
into Malic Acid by heating with water at a
high temperature [1]

The differences in character of Fumaric and Maleic
Acids indicate that one of them (probably Maleic Acid)
has the indivisible form Figs 48, 49 or 50, pp 72a and b,
and that Fumaric Acid has the same configuration as or
dinary Malic Acid and ordinary Tartaric Acid If this be
so, the oxidation of Fumaric and Maleic Acids and the
production of the two forms of Tartaric Acid would be
accounted for   Fumaric Acid however has never been
divided into dextro and lævo forms   A similar absence
of optical activity is observed in ordinary Crotonic
Acid and Succinic Acid

The models which at first sight appear most suitable
to represent Fumaric and Maleic Acids are Nos 48 and
49, which have somewhat similar forms and can easily
be converted and re converted from one form to the
other   It would be satisfactory if we could assign the
two faces occupying the opposite sides of the concavity
to the two unoccupied faces of the molecule, but if this
is done the formulæ of these acids would have to be
altered to

$$
\begin{array}{ccccc}
\text{O} & & \text{H} & \text{H} & & \text{O} \\
\diagdown & & | & | & & \diagup \\
-\text{C}-&\text{C}-&\text{C}-&\text{C}-& \\
\diagup & & | & | & & \diagdown \\
\text{O} & & \text{H} & \text{H} & & \text{O}
\end{array}
$$

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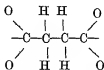
[1] Holleman—" Text Book of Organic Chemistry," Fifth
Edition, p 212

and there would be difficulty in arranging for the acid radicle COOH   It is not improbable that the two opposing sides of the concavity are occupied by the acid radicle and that the unsaturated faces are to be found on the two middle carbonoids

On treatment with sodium amalgam and water, both acids would be broken in the middle at the position of the so-called double bond, and when reunited might produce a new form, say Fig 48, which would easily take up two atoms of Hydrogen with production of Succinic Acid

No decision as to the models of Fumaric and Maleic Acids can however be made at present

Of the Reactions enumerated above, Nos 3, 4 and 5 seem to indicate that the arrangement of the carbon framework of these acids can easily be changed from one form to another   We shall now proceed to consider the extent of these intra-molecular changes

It has already been pointed out, p 79, that the addition of one carbonoid to the two tri carbonoids which are associated as object and image, Fig 44a and b, p 72a, may produce six different forms of tetracarbon oids, and that in some cases the group loses altogether its optical activity and produces one of the forms of carbonoid aggregates which is not associated with optical isomerism

Similar effects can be produced by changes in the positions of the carbonoids in the groups of Tetra-carbonoids shewn on p 72b   Fig 46 (a) can readily be changed into 46 (b), Fig 51, p 96, is a diagramatic representation of 46 (a) consisting

of two Ethyloids, united at the dotted line a—b,
which represents a possible line of fracture ¶
then the molecule be broken along this line and the
two Ethyloids are turned as if the line a—b were a
hinge, then the face (c) would approach face (d) until
a reunion of the two Ethyloid groups would take place
by the attachment of (c) to (d)

By this means a similar molecule would be pro-
duced, but it will have the reverse configuration, see
Fig 52
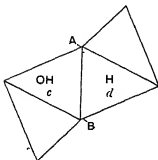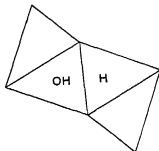
          Fig 51   Fig 52

Some alteration in the position of the attached
Hydrogen and Hydroxyl will be necessary, but this
should not be difficult, if the forces at work on this
molecule are sufficient to break the carbon chain along
the line A—B

The position of the two acid groups COOH will re-
main unaltered

This change corresponds to what may be expected
to take place when Dextro Malic Acid is converted into
the lævo modification

A diagram of the model 46a is shewn below
See Fig 53   If the end carbonoid marked x
shifts its position to the face y by revolving around the
point $*$ so that b is at the point C and A at the
point b, an entirely new figure, No 54, is produced,
which unlike Fig 46, is free from enantiomorphism, and
both 46a and 46b can thus be readily changed into
Fig 54
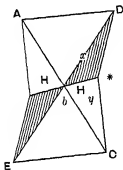
Fig 53   Fig 54
(See also Fig 50, p 72a)
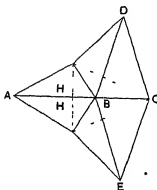
The only change in the attached atoms is the
removal of Hydrogen from the face y to a similar
position on that face of the adjoining carbonoid pre-
viously occupied by the carbonoid x

The solid angle which separates this face from the
face y is very obtuse, and the sliding of the carbonoid
from one position to the other can very easily take
place

This change corresponds to what may be supposed to take place when the ordinary forms of Malic Acid dextro and lævo are both changed into Fumaric or Maleic Acid

Many other similar transformations can take place by the change of linking of the carbonoids or Ethyloids with comparatively slight changes of position in the carbonoid aggregate   These can best be discerned with the help of a model, when the changes can be traced and the results seen, but sufficient has been shewn to illustrate the readiness with which the form of the molecule may be changed and the enantiomorphism lost or regained

Sufficient has perhaps been stated to justify the view that the new theory ought not to be put aside on the ground of the changes of form required in the carbonoid aggregate

It may fairly be argued however that the well known stability of the carbon chain renders it unlikely that a change of structure will actually take place, such as has been proposed   In this connection it is pointed out that in certain circumstances a carbon chain may be broken and the molecule decomposed—as an instance take Trimethyl Carbinol

$$H_3C$$
$$H_3C-C\ OH$$
$$H_3C$$

the Carbon framework of this substance being represented in Fig 50, p 72a, which on oxidation breaks up

into substances with a smaller number of carbon atoms
Oxidation of tertiary alcohols generally results in a
breaking up of the molecule

Another case of intramolecular transformation will
be found in the formation of Pinacoline

$$(CH_3)_3 \quad C \quad CO \quad CH_3$$
$$(i) \quad (y)$$

from Pinacone $(CH_3)_2$ $C(OH)$—$\overset{OH}{\underset{CH_3}{\overset{|}{C}}}$—$\overset{}{\underset{}{CH_3}}$
$$(i) \qquad (y)$$
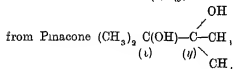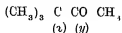
here the methyl group is moved from C in Pinacone to C
in Pinacoline $\qquad$ (y) $\qquad$ (i)

According to the models (and assuming that the
position of the carbonoids is accurately represented by
the formulæ) this change is due to a movement of a
carbonoid, which involves considerable alteration in its
position in the molecule and results in a different con-
figuration of the carbon framework.

With regard to molecules containing five or more
carbon atoms, it must be pointed out that among the
amyl alcohols there are two—secondary Butyl carbinol
and Methyl Propyl Alcohol—which are active com-
pounds

Of the other amyl alcohols there are four in which
the carbon frame-work is such that no enantiomorphous
configuration is likely, viz —

Isobutyl carbinol
Methyl isopropyl carbinol
Dimethyl ethyl carbinol
Tertiary butyl carbinol

Diethyl Carbinol appears to have a form which is inactive, although other forms can be designed which would produce active isomers, but the latter appear to be probably unstable

There remains the normal primary Amyl Alcohol, which appears to consist of a normal chain of Carbon with the Hydroxyl attached to the end carbon

A simple chain of five carbonoids will have the spiral formation and should exist in two active isomers The fact that the Hydroxyl group is attached to the end carbon

$$\begin{array}{ccccc} \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\ | & | & | & | & | \\ \text{H--C--C--C--C--C--OH} \\ | & | & | & | & | \\ \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \end{array}$$
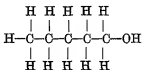
may render the two isomers inseparable, it seems doubtful if any means at present exists for removing the Hydroxyl from one of the two isomers in preference to the other

With regard to substances containing six or more carbon atoms, arranged in a normal chain, such molecules should exhibit the spiral structure, and therefore should give rise to optical isomerism

Compounds of six or seven carbons may exist in which the position of branched chains may prevent the formation of a spiral chain, such as for instance —

$$\begin{array}{ccc} \text{C} & & \text{C} \\ \diagdown & & \diagup \\ & \text{C--C--C} \\ \diagup & & \diagdown \\ \text{C} & & \text{C} \end{array}$$

In this case, if the compound is balanced so that the attached atoms or groups on either hand are equal, no optical activity will arise, but in the case of a normal chain C—C—C—C—C—C—C—the carbonoids will be arranged in a spiral form

It may be asked what form are we to assign to the normal chains in the well known Homologous series, the Paraffins, Olefines, Alcohols and Ethers

With regard to the Paraffins, the normal chains of three or more carbons should be arranged in a spiral formation, and the compound should exist in three isomeric forms, d, l, and racemic   Is this the case ?

According to Holleman,[1] optical activity exists in the Petroleums[1] when in the natural state   The particular substance which gives this character to the mixture of Hydrocarbons which make up Petroleum does not appear to have been isolated, and the optical activity may be due to some impurity   If, on the other hand, it is established that some of the Paraffins and Olefines exist in two active isomers, the above question will be satisfactorily answered

Some of the higher Alcohols may be expected to shew optical activity, but the peculiar configuration of the Ethers does not seem to lend itself to this form of Isomerism

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[1] Holleman—" Text Book of Organic Chemistry," Fifth Edition, p 40

CHAPTER X

CONDENSED RINGS

The consideration of those compounds which according to the usual formulæ comprise two or more condensed Rings is a matter of special importance, because it is impossible to prepare combinations of Benzenoids which will represent these formulæ Two Benzenoids in the same plane cannot be united by having two carbonoids common to the two rings

At the outset this fact appeared to present a difficulty in the way of the acceptance of the theory of Atomic Form

With regard to Naphthalene $C_{10}H_8$, the following is the usual formula
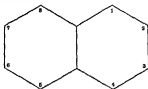
The consideration of the oxidation of α Nitronaphthalene and of α Naphthylamine and the oxidation of Quinoline to Quinolinic Acid on the one hand, and to a derivative of Anthranilic Acid on the other, appeared to justify the acceptance of the recognised formula for Naphthalene

Moreover, the fact that Isoquinoline on oxidation yields a mixture of Phthalic Acid and Cinchomeronic Acid seems conclusive on this point
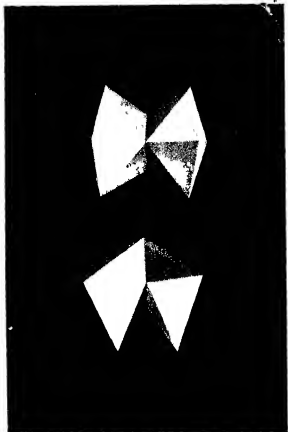
Fig 55

NAPHTHALENE

Fig 58

O Xylylene showing Di ethylene Group

Cinchomeronic   Phthalic
Acid   Isoquinoline   Acid
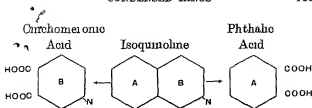
The formula for Isoquinoline is C_9H_7N, and the Nitrogen atom forms part of the Ring B which persists in the formula for Cinchomeronic Acid, while Ring A, in which there is no Nitrogen, gives rise to Phthalic Acid

Further consideration of the models shews however that an arrangement of 10 carbonoids can readily be made, in which two groups of four carbonoids each are united by an ethyloid as in photograph shewn in Fig 55, p 103a

It is suggested that this photograph gives a faithful representation of the formula of Naphthalene, which may be represented thus —

$$C_{10}H_8$$
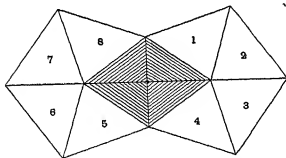
Fig 56

NOTE —This diagram shews the central Ethyloid group, which in fact is covered by the two di ethyloids

Naphthalene would thus appear to have the same
configuration as the tetracarbonoid shewn in Fig. 49,
p 72b, and which will in future be described as a di-
ethyloid

Naphthalene may be compounded of five ethyloids
arranged so as to produce one molecule of the form
shewn above   As explained under Cyclo-pentane,
chapt XI the group of two ethyloids or four carbonoids
shewn in Fig 49, leaves a gap between the two end car-
bonoids approximately equal to another carbonoid   It is
this gap that is filled by one of the carbonoids of the
central ethyloid group, the other carbonoid of the
ethyloid carrying another Di-ethyloid group similar to
the one first mentioned and depicted in Fig 49

The gap in the Di ethyloid Ring fits almost exactly
to the carbonoid and will certainly make a stable
arrangement almost equal in stability to a Benzene
Ring

. The eight Hydrogen atoms fall naturally into their
places 1 to 8 as marked in the above formula, and there is
no opportunity for attaching any other Hydrogen atoms
except on the other side of the molecule, which, as in
Benzene, is unsaturated

This formula is also applicable to isoquinoline
and accords with the results of oxidation as shewn
above   When the isoquinoline molecule is broken up
one di-ethyloid is removed and the other di ethyloid
plus the ethyloid which is common to the two rings will
form a Benzene or pyridine Ring without changing
the positions of the attached Hydrogen, but a general
rearrangement of the carbonoids is necessary   The

changes necessary to effect this and the positions in the molecule retained by the attached Hydrogen are difficult to describe, but can readily be appreciated with the help of the models

The monosubstitution products of Naphthalene are divided into two series, α and β, the former being cases where the substitution takes place on a carbon atom directly linked to the adjacent Ring, 1, 4, 5 or 8, and the β series representing those in which substitution takes place at 2, 3, 6 or 7, see formula, on page 103

The formula for Napthalene, Fig 56, p 103, shews that the occupied faces are divisible into two series according to the position of the carbonoids, Nos 1, 4, 5, 8, being situated close together in the centre of the molecule, and No 2, 3, 6, 7 occupying positions further removed from the centre

The synthesis of Naphthalene from Benzene Vapour by passing it through a *white* hot tube is quite consistent with the configuration shewn above

It is clear that the rise of temperature involved in this synthesis is sufficient to break up the Benzene Ring into three Ethyloids, many of which will recombine in a different way so as to produce the molecule of Naphthalene We have already noticed the great stability of the Ethyloid, and it is improbable that the rise of temperature in a *white* hot tube will be sufficient to break up the Ethyloids into single carbon oids, if, however, this breaking up should take place, the Ethyloids would be re-formed as soon as the temperature is lowered

H

Another synthesis of Naphthalene is from *o-Xylylene*
Bromide

$$C_6H_4 \begin{array}{c} CH_2Br \\ \\ CH_2Br \end{array}$$

This compound, when freed from the two Bromine
atoms, presents the curious feature that the two CH_2
groups in combination with two of the carbons of the
Benzene Ring form a group of four carbons and in
representing this group by our models, we find that it is
arranged relatively in the same way as the Di ethyloid
Group, see the photograph, Fig 58, p 103a

o-Xylylene may therefore be represented by the
following formula

Di ethyloid
Group
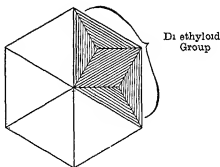
Fig 57
The dotted lines represent the probable lines of fracture

The reactions which subsequently take place during the synthesis of Naphthalene involve the use of the very large molecule of tetra disodio ethane-tetra carboxylate and appear to be sufficient to disturb the stability of the Benzene Ring causing a rearrangement in the form required to produce the configuration shewn in Fig 55, p 103a

It is also noticeable that it is only the *ortho* compound which is capable of producing the di ethyloid group In the meta and para compounds no such group will arise, this feature also corresponds with the fact that it is only the *ortho* xylylene that can be used to synthesize Naphthalene

Another synthesis of Naphthol, a derivative of Naphthalene, is from Phenyl Vinyl Acetic Acid There are five acids isomeric with Vinyl Acetic Acid of the formula $C_4H_6O_2$, but there are only four formulæ available for representing them It seems probable that one or more of these acids differ from the other isomers in the arrangement of the carbon framework, and may have the form of the di-ethyloid If this be the case the formation of Naphthalene from this compound is a confirmation of the suggested configuration

The oxidation of Naphthalene to Phthalic Acid seems to point to the existence of a Benzene nucleus as part of the molecule, this however is not certain

The following quotation from Cohen's *Text Book of Organic Chemistry* points to the possibility of a constitution for Naphthalene in which the constituents, although not forming a Benzene Ring, are readily convertable into such a group —

> [1]" Does the formation of Benzene derivatives from Naphthalene, and both Benzene and Pyridine derivatives from quinoline and isoquinoline, necessarily imply the pre existence of these nuclei in the original compound ?
>
> " Although at first sight an affirmative reply to the question appears the most simple and obvious one, Bamberger has shewn that there are many experimental facts which are opposed to it, and he prefers to regard all three compounds as represented by a ring of 10 atoms, in which the 4th Carbon or 3rd Nitrogen bonds as the case may be, are directed 'towards the centre of each nucleus "

The Theory of Atomic Form does not make it necessary to account for all the unoccupied faces of the molecule, and allows for some of these to remain unsaturated both in the Benzene Ring and in Naphthalene, the position of the molecules in space and their rotational movements being considered to be sufficient to account for the unsaturated condition of the molecule

---

[1] Cohen—" *Organic Chemistry*," 2nd Edition, Part III , p 283

ANTHRACENE AND PHENANTHRENE $C_{13}H_{10}$.

The recognised formulæ for these two compounds are—

Anthracene

Phenanthrene

OH = CH

or
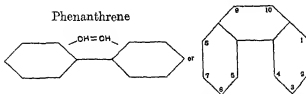
Except as regards the first formula for Phenanthrene there is a difficulty in representing these formulæ by the models of the Benzene Ring, as they involve the *condensed* Ring system

As regards Anthracene, a simple formula of two benzenoids linked together by two carbonoids gives a model of this compound, in which, however, there is no hydrogen attached to the two central carbonoids which form the link between the two Benzenoid Rings See the following formula
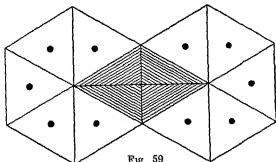
Fig 59

The spots represent attached hydrogen

The synthesis of anthracene from benzene and tetra-bromo-ethane is consistent with this model On removal of Bromine from the tetra-bromo-ethane there remains a single Ethyloid which without change can form the link between two Benzene rings, but which would have to be broken up into single carbons in order to link together these two rings in *two* places

The Hydrogen attached to this Ethyloid appears to be removed by the Bromine , this may quite probably be the case, leaving five atoms of Hydrogen in attachment to each of the two Benzene rings   This arrangement of the Hydrogen is at least quite as probable as that proposed in the condensed ring formula

The production of Anthraquinone by oxidation of Anthracene will result by the attachment of two oxygen atoms to the two Benzene rings, reducing the number of Hydrogen to 8

The point of difficulty is whether the link consists of two carbons in the ortho position or not , the synthesis of Anthraquinone from Phthalic Anhydride and Benzene may be considered as furnishing proof of the existence of two carbons in the ortho position, but the evidence does not appear to be conclusive on this point

------

PHENANTHRENE

The existence of a condensed ring in the constitution of Phenanthrene is certainly a matter of doubt

In Stilbene $CH-C_6H_5$
         (a) $\|$
             $CH-C_6H_5$

the two carbons which connect the two phenyl groups are not linked to them in *two* positions having regard to the number of Hydrogen atoms attached to these groups   The red hot tube enables the compound to throw off two Hydrogen atoms, which may be withdrawn from the link C_2H_2 or from the rings, reducing them to C_6H_4, but there is no evidence that the C_2H_2 is linked to two places in each of the rings, and the facts with regard to the addition of Bromine and Oxygen to the link seem to negative the view that there is a third ring in Phenanthrene

It is suggested that this compound may be a diphenyl with two carbons attached, in which case the new formula for Phenanthrene would be expressed thus —

Carbonoid   (β)   Carbonoid

Benzenoid   Benzenoid

Fig 60

$CH-C_6H_4-C_6H_4-CH$
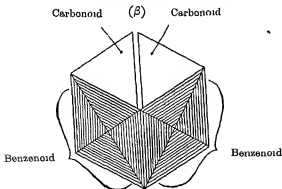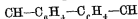
When Stilbene Vapor is passed through the red hot tube it is suggested that a fracture takes place at the point (a) and that the two phenyl groups after losing two Hydrogen atoms, unite to form a group of a diphenylic character

$$
\begin{array}{cc}
CH & CH \\
| & | \\
C_6H_4 & \!\!\!\!\!\!\!—\!\!\!\!\!\! C_6H_4
\end{array}
$$

There is no attachment between the two carbonoids at (β) which meet at their edges and the molecule would be likely not to be very stable It melts at 96°, Anthracene 213°, and dissolves in Alcohol more readily than Anthracene

We do not consider however that in this case the carbonoid model accords in all respects with the molecule of Phenanthrene, and we think that the form of the model must be reserved for further consideration

Other models can be prepared representing in different forms the complete series, from Naphthalene $C_{10}H_8$ to Chrysene $C_{18}H_{12}$, but they do not accord with the accepted formulæ, and there are some points of difficulty in connection with them which cannot at present be explained It therefore appears to be best to await further knowledge in connection with the subject of this chapter

CHAPTER XI

CYCLIC COMPOUNDS

The Heterocyclic compounds, containing other elements such as Nitrogen, Oxygen, Sulphur, etc., are considered to be outside the scope of this work, which is confined to carbon compounds

The substances with which we propose to deal are therefore —

> Cyclo-Propane
> Cyclo-Butane
> Cyclo-Pentane
> Cyclo-Hexane

also the higher cyclic compounds, Cyclo Heptane and Cyclo-Octane

CYCLO-HEXANE   This is a Benzene derivative, represented so far as the carbon framework is concerned by the Benzenoid which has already been discussed in Chapter III

It is produced by mixing Benzene vapor with Hydrogen over finely divided Nickel at a temperature of over 150°, also by the action of Palladium black on Benzene and Hydrogen, by this means combination of Benzene and Hydrogen takes place—the compound clearly contains a six membered ring, and its configuration is well-known

Phloroglucinol and Hexahydroxy Benzene may also be considered as being Benzene derivatives and having the Benzenoid configuration

In the cases of some other derivatives containing six carbons, the cyclic form is not so clearly indicated, and it seems possible that some of these compounds may be unsaturated—it is unnecessary, however, to decide this point, as our models provide for cyclic formation in the case of all compounds containing five or six carbon atoms

CYCLO-PROPANE   With regard to cyclo propane and cyclo-butane, the carbonoid aggregates are unable to form closed rings of 3 or 4 carbonoids only

If we adopt the theory that as the carbon chain is lengthened it tends to bend round, so that its ends approach each other, until the compound containing five atoms is reached, the configuration of the cyclic compounds of 3, 4 or 5 carbons can be illustrated by the following scheme —
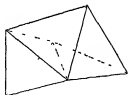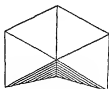
Fig 61   Fig 62
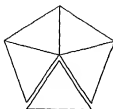
Fig 63a   Fig 63b

But these figures do not represent true cyclic configura-
tions except in the case of the second form for Penta-
carbonoid, Fig 63b   In this form we have a figure
which is in reality a closed ring   It has already been
referred to in Chapter X in connection with Condensed
Rings   Although the fifth carbon atom does not fill
the space in the Ring with the exactitude of the carbon
atoms in Benzene, yet it is almost a precise fit, and one
which clearly prevents the existence of any unoccupied
faces and must render the molecule stable

   In Fig 63a, there is more opportunity for instability
in the structure, but the two opposing faces at the ends
of the chain are in such a position that they will probably
remain unoccupied by any atom larger than hydrogen

   The stability of cyclo pentane and its derivatives
is well-known ; it does not yield any addition product
with Bromine, and is as stable towards Nitric and Sul-
phuric Acids as a saturated Hydrocarbon   It also re-
sists boiling with Hydriodic Acid, and is the most stable

of the cyclo-paraffins   From the results now available
it may be said that in compounds of five or six carbons,
we may have rings of much greater stability than those
where there are a greater or less number of carbon atoms
in the molecule

Our models shew that it is only the aggregates of
five or six carbonoids which are capable of true ring for-
mation, and that of the two forms the Benzenoid is the
most stable, while the model of cyclo-pentane, Fig 63b,
approaches it in stability very nearly

Let us now consider the evidence in favour of ring
formation in the cases of cyclo propane and cyclo-butane

The synthesis of the former is as follows —

$$\text{Allyl Alcohol} \qquad \underset{|}{\text{CH}_2}-\underset{|}{\text{CH}}-\text{CH}_2\text{OH}$$

$$-\text{OH} \quad + \text{ Br}$$

$$= \underset{|}{\text{CH}_2}-\underset{|}{\text{CH}}-\text{CH}_2\text{Br}$$

$$+ \text{ H Br} \qquad \text{CH}_2\text{Br}-\underset{|}{\text{CH}}-\text{CH}_2\text{Br}$$
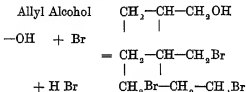
by the action of sodium 2Br, are removed, leaving

$$\text{cyclo-propane} \quad \underset{|}{\text{CH}_2}-\underset{|}{\text{CH}_2}-\underset{|}{\text{CH}_2}$$
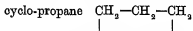
this substance is not identical with propylene—

$$\underset{|}{\text{CH}_2}-\underset{|}{\text{CH}}-\text{CH}$$

It has been assumed that the formula of cyclo-propane
should be written thus

$$\text{CH}_2\underset{\diagdown}{\overset{\text{CH}_2}{\diagup}}\Big|_{\text{CH}_2}$$

but if this synthesis is critically examined in the light of the theory of Atomic Form, there will be found nothing to support the view that the above "ring" formula is correct

Those who adopt the theory of Atomic Form will also adopt the view that in carbon chains faces may be unsaturated, but such unsaturated faces will be always in *pairs*, either on adjoining carbonoids or on the faces occupying corresponding positions at the two ends of the carbon chain, the existence of these pairs being due to the configuration of the carbon chain as explained in Chapter V under the head of "Law of Even Numbers"

It has been already stated that the idea of a double bond must be rejected, and a pair of unsaturated faces substituted, the existence of unsaturation in these cases being justified by the consideration of the position of the faces in the chain and the probable axis of rotation of the molecule, moreover the readiness with which addition products are produced amounts almost to proof of the unsaturated character of these pairs of faces

In the case of cyclic compounds—cyclo-propane and cyclo-butane—it has been impossible to adopt the idea of a double bond, and it is submitted that in these cases chemists have had recourse to the idea of cyclic formation in order to satisfy the current theories in regard to saturation and having regard to the differences in Chemical and Physical Characteristics between the cyclic compounds and the isomeric Olefines

If we adopt the theory of Atomic Form, we assume that these unsaturated faces are available for the formation of addition products   Cyclo-propane is acted upon

by Hydrochloric, Hydrobromic, and Hydriodic Acids
and also by Sulphuric Acid, but it does not appear to
be acted upon as easily as its isomeric Olefine, for
instance, it is not attacked by Permanganate, and
Bromine acts upon it slowly

It will be seen on referring to Fig 44a and b and 45,
p 72a, that either of these figures may be chosen to repre-
sent cyclo-propane   If we adopt Fig 44a and b, we shall
have to consider this substance as being a mixture of
the right and left handed forms, this is possible, but
the two active isomers have not so far been separated
If we adopt Fig 45, we must not assume that the two
co-planar faces at the base of the figure are unsaturated,
as if this were the case, two molecules would immediately
join to form a Benzene derivative—cyclo-hexane

There seems no reason why we should assume that
the two co-planar faces are unsaturated   The position of
the Hydrogen may be as shewn in the following diagram

Fig 64

In the two isomeric forms, Fig 44a and b, we may
assume that it is the two faces on the opposite sides
of the concavity that are unsaturated, this would
accord better with the features of cyclo-propane, as
there might be more difficulty in attaching addition
products to these two faces than there would be in the
case of the isomeric Olefine or in the case of Fig 45

The differences in chemical and physical character istics which separate propylene and cyclo-propane are not very great, the principal difference being in regard to Potassium permanganate, for while Propylene reacts with this substance in dilute solution in contact with Sodium Carbonate, Cyclo propane does not react with Potassium permanganate Both compounds form addit ion products with the Halogen Acids and with Sulphuric Acid, their Boiling points are reported as—

Propylene—48°
Cyclo-Propane—35° calculated

Propylene adds on Bromine readily, but Cyclo propane *slowly*

It must be admitted that there is considerable difficulty in deciding upon the configuration of cyclo propane as also in deciding which of the two Figs 44 or 45 should be assigned to it

It is submitted that if Fig 45 is adopted the differ ences in the structure of the carbon framework are sufficient to explain the differences in Chemical and Physical Characteristics, and if Fig 44 is adopted the position of the unsaturated faces on the opposing sides of the concavity would also materially affect the re activity of the compound

CYCLO-BUTANE This substance can be synthesized from Cyclo-Butyl-Carboxylic Acid, but we do not find any direct evidence of the existence of a cyclic formation

It can be converted into cyclo pentane, but there does not appear to be any evidence of the conversion of any of these substances into compounds containing a Benzene Ring

CYCLO-PENTANE is synthesized from Calcium Adipate, but there is no direct connection between this substance and compounds containing the Benzene Ring—the existence of a true ring in this compound appears open to doubt Either of the two possible configurations shewn on page 115 may be adopted, and in the first case the two faces on opposite sides of the concavity will be so situated that addition products will be impossible The second configuration, Fig 63b seems, however, to be more in harmony with the stability of the substance

CYCLO-HEPTANE AND CYCLO-OCTANE In these compounds it is suggested that instead of a cyclic configuration, unsaturation is indicated, the unoccupied faces being situated at the opposite ends of the carbonoid aggregate

CHAPTER XII

CONCLUDING OBSERVATIONS

The question of whether any other Investigator has already propounded any Theory of Atomic Form in connection with the Carbon Atom naturally deserves consideration

It appears that some attempts have been made in this direction by Chemists abroad, but the papers on the subject are only to be found in Foreign Journals or Publications and no particulars are to be found in those Text Books in this country to which the Author has access

Much of what appears in the foregoing pages is the result of a study of models of the Carbonoid and its aggregates, and it is difficult to explain by drawings alone all the features of these aggregates, as it is only by inspection of the models and the groups of models that their peculiar configurations can be realised   It is submitted that some justification of the Theory of Atomic Form is to be found in the facts set forth in the preceding chapters, and that this view is supported by the way in which the carbon framework of the principal formulæ in which carbon takes a part are represented by groups and aggregates of the carbonoid

I

It is remarkable that the characteristics of the Ethylene group, and the Benzene Nucleus should be represented by models of carbonoid aggregates, and that, at the same time, the right- and left-handed Isomerism and Law of Even Numbers should find their illustration, and possible explanation, in the models of carbonoid chains, while at the same time the crystalline forms of solid carbon are fully accounted for Triphenyl-methane, Condensed Rings, and Cyclic Compounds are considered, and suggestions are made with regard to the structure of these compounds

The consideration of the crystallization of carbon compounds, such as Carbon Dioxide, Benzene, Naphthalene, etc, may lead to difficulties If the crystal form depends upon the configuration of the molecules of which the compound is composed, the models of the carbon framework should be of such a form that they can be built up into a space lattice suitable for the required crystal Very little progress has however been made in this direction

In the case of a single element where the form of the atom is assumed, there should be no difficulty in forming a suitable space lattice, but where more than one element is involved in the molecule, as in the Hydrocarbons, we are met with the difficulty that we do not know the form of the other element nor what effect the Hydrogen or Oxygen of the compound may have on its power of crystallisation

It is clear, however, that Oxygen possesses an unique power of linking together other elements so as to form crystalline compounds, the carbonates, silicates, nitrates, phosphates, sulphates and other compounds

prove the large number of substances, with very
definite crystalline forms of which Oxygen forms a part

It will be observed that throughout this book sym-
bols representing double bonds have not been generally
employed ,— unsaturated molecules being treated as
having unoccupied faces   It is of course impossible for
any geometric solid figure to be united to another figure of
the same or similar form by more than one of its faces,
but it is quite likely that where the attached atom is
of large size, compared with the atom to which it is
attached, the base of the attached atom may extend
beyond the face of the " nuclear " atom and may prevent
the occupation of an adjoining face   The question of
whether a particular face of an atom is available for
occupation by another " attached " atom will depend
upon the position which this face occupies in the mole-
cule—the configuration of both the " nuclear " and the
" attached " atoms, and sometimes on the axis of
rotation of the molecule   The introduction of the idea
of geometric form, provides new possibilities affecting
the valency of the atoms

With regard to the formation described as "con-
jugated" Double Bonds, of the form C=C—C=C or

$$
\begin{array}{c}
\;\;|\;\;\;|\;\;\;|\;\;\;| \\
H-C-C-C-C-H \\
\;\;|\;\;\;|\;\;\;|\;\;\;| \\
\;\;H\;\;H\;\;H\;\;H
\end{array}
\qquad \text{the addition of Bromine}
$$
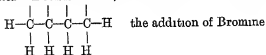
takes place at Nos 1 and 4, thus

$$
\begin{array}{c}
\;\;\;\;Br\;\;\;\;\;\;\;\;\;\;Br \\
\;\;\;\;|\;\;\;|\;\;\;|\;\;\;| \\
H-C-C-C-C-H \\
\;\;\;\;|\;\;\;|\;\;\;|\;\;\;| \\
\;\;\;\;H\;\;H\;\;H\;\;H
\end{array}
$$
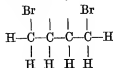
the so called double bond being removed to the pair of
atoms, 2 and 3 above, this seems probable by reason of
the size of the Bromine Atom, which in some circum-
stances might be prevented from occupying the faces
of adjacent carbonoids

The existence of the four unoccupied faces in juxta-
position is accompanied by an exaltation of the mole-
cular refraction which disappears on the removal of
the pair of unoccupied faces to the middle of the molecule

In partial explanation of these features we notice
that a tetracarbonoid model when viewed from one
side, which we will call the front of the model, presents
two pairs of co basal faces, Nos 1—2 and 3—4, see
Fig 46, p 72b, but on the occupation of Nos 1 and 4,
the remaining faces 2 and 3 do not present a pair of
faces in a satisfactory position to one another, the
pair being separated by a considerable space

Another view of the model from the back shews
four faces arranged as shewn in Figs 51 and 52,
p 96

On the occupation of the two faces at the top
and bottom of the figure, being Nos 1 and 4 in the
foregoing formula, there remains a pair of co-basal
faces (unoccupied) in the middle, marked c and d in
Fig 51, which may fairly represent the double bond in
the centre of the molecule

Without being confident that this is the correct
solution of the problem, the carbonoid model shews

how a case of four adjacent unsaturated faces may be re
solved into a single pair of faces on adjacent carbonoids
united by the same base, and occupying the middle of
the formula

It is possible to design forms for the various ele-
ments with any number of faces from 4—excepting 7—
up to at least 8, and the positions of these faces
could be such as readily to give either 3 or 5
" available " faces, 4 or 6, etc, and as we have
already shewn, the faces available for attachment may
be limited to 1 or 2

With regard to Cyclic Compounds, the point at
issue in connection with these compounds (except those
containing five or six carbons) is whether they are true
ring structures or whether they have some other con-
figuration, differing from the open chain compounds,
in the form of the carbon framework and probably
also in the arrangement of the attached Hydrogen
It is submitted that the variety of form of carbonoid
aggregates enables a different carbon framework to be
allotted to these compounds and thus provides for the
differences of character which are observed

In compounds containing more than six carbons
symmetrical groups of carbonoids can be constructed
which differ from the spiral chains allotted to the open
chain compounds, but which may nevertheless represent
cyclic compounds   Here again the variety of form
obtainable by different combinations of carbonoids is
noticeable

The Theory of Atomic Form must accord with the classification of the Elements under the Periodic Law, and it is suggested that the various groups and sub-groups into which the Elements are divided under this law are represented by different geometrical solid forms which are either the same or similar for atoms comprised in the same group

In some cases the form may be the same, but the size of the atom may be different owing to an enlargement of its dimensions   In other cases while the main features of the geometric form are retained and the number of faces remains the same, a change in one or more of the dimensions will produce a somewhat different figure with a larger size   A complete change of form including a larger number of faces may represent a change from one group to another

In order to verify these assumptions it is necessary that the forms should be ascertained of a considerable number of the Elements, including those belonging to the same group, a work of considerable difficulty

Let us consider the case of Silicon—the Element so closely allied to Carbon and occupying the next place to it in Group IV in the Table   It seems probable that Silicon may have a similar form to Carbon, with a proportional enlargement of its dimensions

It will be remembered that the face of the carbonoid is an isosceles triangle, where A—D = B—C   Fig No 9

Any alteration of A—D will result in an alteration of the size of the solid figure without altering the form of the atom

It is immaterial what the unit of measurement may be. Let us assume that A—D, or B— C = 24, then the volume of the Carbonoid will be 1995 36

Let us assume that the Siliconoid has a base and perpendicular enlarged by one-third, making it 24+8 = 32, then the volume of the Siliconoid will be 4729 6853

The volumes of these two figures should stand to one another in the same ratios as the atomic weights of Carbon and Silicon   The following is the result —

Mass of Carbonoid	Mass of Siliconoid	Atomic Weight of Carbon	Calculated Atomic Weight of Silicon
1995 36	4729 685	12	28 44

The atomic weight of Silicon in the latest estimation available is 28 25, an earlier estimation gave 28 4

The closeness of this result is noteworthy, but it must be remembered that it has been obtained by an arbitrary addition of one-third to the base and perpendicular of the carbonoid, a simple proportion, but one for which there is at present no authority

Attempts to arrive at the mass of Titanium by a similar increase in the dimensions of the carbonoid, have not shewn any agreement with the Atomic Form, but this element cannot be regarded as closely associated with Carbon or Silicon

While an attempt has been made in this book to elucidate the form of the carbon atom, much difficulty and uncertainty surrounds the theory of Atomic Form when applied to other elements, and the consideration of these problems has necessarily been deferred

Any attempt to apply the Theory of Atomic Form to the elements generally, brings us face to face with problems of some difficulty

With regard to Atomic weight, Valency, and certain other properties, the first seven elements in the Periodic Table shew a sequence of some regularity, which points to the existence of a relationship between them by which each of these seven typical elements may be considered as dependent to some extent upon those which precede and follow it in the table, as for instance in the case of the following pair of triplets

| M X | Lithium | 7 | | M X₄ | Carbon | 12 |

M X	Lithium	7		M X$_4$	Carbon	12
M X$_2$	Beryllium	9 1		M X$_3$	Nitrogen	14
M X$_3$	Boron	11		M X$_2$	Oxygen	16

but notwithstanding this interdependence, the characters of these elements differ widely and in many important points—particularly melting point

The Fluorine group starting at 19 stands alone, but appears to be related to the six preceding items

There is another triplet—Iron 56, Cobalt 59, Nickel 58 7, which fills an unique position in the table, and cannot be considered as being related in any similar way to the other members of the table, and in addition there is the Helium-Neon group, making eight groups in all which start from elements of low Atomic weight, and three start from Iron and its congeners Hydrogen stands alone and cannot very well be considered in our present state of knowledge as being associated with any one of these groups

Can each of the interdependent elements have a separate geometric form of atom, on which its characteristics depend ? If so, there must be some principle involved which is applicable to all the eight elements and which ordains the regularities which are observable   At present we do not understand how these separate Forms can be allied to one another so as to produce the regular increments of Atomic weight, and the regular sequence of Valency

The advances from the first to the second period in the table are associated with an increase of Atomic Weight which approximates closely to 16 in each case, with, however, this feature, that the principal divergencies from an increase of 16 is found in the middle member of each triplet   Beryllium increases by a little over 15 to form Magnesium, and Nitrogen by about 17 to form Phosphorous

From the second to the third period the increment is about 16 for the first triplet and about 20 for the second   Such increases cannot be reduced to any regular proportion of the Atomic weights with which the group commences

In the case of Silicon, we have found that 1/3rd added to the dimensions of the Carbonoid produces a solid figure with the Atomic weight of Silicon, but if we were in a position to make a similar calculation for Oxygen, we should probably have to employ some entirely different proportion and so on for each member of the eight groups

If, therefore, each of the elements has its own geometric form, how can the mass of the Atom be enlarged by the same quantity in each case, in order to produce the next item in the group ?

Another peculiarity of these groups is to be found in the way in which they divide into two series thus

$$K\ 39—Rb\ 85\ 4—C_s\ 133$$

Li 7—Na 23

$$Cu\ 63\ 6—Ag\ 108—Au\ 197\ 2$$
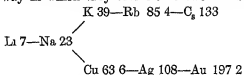
No explanations of these curious relationships are at present available

Although these increases are generally so regular that the elements almost always retain the same order in the 3rd and 4th periods, they are evidently independent (so far as Atomic weight is concerned) of the groups that precede and follow them in the Periodic Table, the differences between consecutive elements becoming both greater and less in the later periods, and in two cases, Tellurium and Argon, the Atomic weights advancing beyond the position of the next group above it

It is submitted that the Table of Atomic weights must be regarded as a record of a series of groups starting from the 11 elements above mentioned

It is suggested that three problems lie before us viz —

(1) What are the relationships existing between the 11 elements referred to above ?

(2) What are the principles which determine the Atomic weights and other characteristics of each item in the several groups ? and in what way are they dependent upon one another ?

(3) What is the nature of the changes of form and
    character which arise with each increment in
    Atomic weight ?

The Theory of Atomic Form postulates that these
problems can be answered by determining the geo-
metric form of each of the 11 elements and by arriving
at the changes in the dimensions and form thereof which
produce the increments in Atomic Weight as we pass
from one series to the next   Such changes may be
produced by aggregations or additions of simpler forms,
or by an increase in dimensions of some part of the
geometric figure or by some other change of form, but
we are still far from being able to present any com-
prehensive scheme or to submit forms suitable for any
of the groups except Carbon

In view, however, of the strong *a priori* grounds in
favour of the view that the elements must possess geo-
metric forms which have been already discussed in
Chapter I , we submit that these problems deserve
further study and consideration

With regard to crystallization, it is suggested that
three different kinds of aggregates should be acknow-
ledged

    (1) The " *Filament* " where the molecules, as in
        Isoprene and the Rubbers, are merely
        linked to one another in a chain of inde-
        finite length

    (2) The " *Network* " where the molecules are cap-
        able of being linked together in the form of a
        network, as in the case of Graphite, but do
        not build up a lattice in three dimensions

(3) The "*Crystal*" where the molecules are built up in a definite geometric form dependent on, although not necessarily similar to, the forms of the atoms making up the molecule

It is suggested that these distinctions should be borne in mind when considering the forms of atoms and molecules

Attention is directed to the argument in favour of the Theory of Atomic Form which is based upon the inability of the present constitutional formulæ properly to represent some of the isomeric forms of compounds of three or more carbons

The present formulæ are unable to represent the form of the carbon aggregates in cases where the isomerism is due to the special configuration of these aggregates   Instances of this kind are to be found in the three forms of Malic Acid and the five forms of Acids of the formula $C_4 H_6 O_5$ when only four are theoretically possible   In other cases where the Isomers are assumed to be represented by different arrangements of the attached Oxygen and Hydrogen, a critical study of the facts indicates that some other and more important differences of configuration are probably the causes of the differences in chemical and physical characters which these isomers display

It is submitted that no satisfactory formulæ can be prepared, so long as the carbon atom is assumed to be spherical in form, and therefore unable to be built up into right- and left-handed forms for the carbon framework of compounds containing three or more carbons

Attempts to get over this difficulty have been made by introducing the *trans* and *cis* formulæ in which the carbons are assumed to be arranged in a special manner relative to one another   The carbon atoms will how ever be unable to do this with any degree of stability unless they are themselves tetrahedra, or unless special and peculiar forces are acting between the spheres   We have no definite knowledge of the forces operating between the atoms of a carbon compound, and give rise to attraction and cohesion, but it is difficult to understand how any such force can act upon a system of spheres in such a way as to produce a stable configuration as depicted in some of our formulæ

The idea that Electronic forces are responsible for the formation of carbon aggregates is not supported by chemical evidence

Such forces are responsible for the behaviour of ions in solutions of electrolytes but they do not play any part in chemical reactions nor exercise directive power over the formation of isomeric compounds

On the other hand, if the tetrahedral form of the carbon atom is adopted, we are placed in possession of a number of different forms of carbonoid aggregates, which enable all these isomers to be adequately represented and the isomerism explained

The *trans* and *cis* formulæ are no doubt useful so far as they indicate that there is a change in the position of the carbon atoms relatively to one another, but they fail to indicate the true positions of the carbons in the molecule or the causes of the differences between the isomers

Much remains to be done before the theory of Atomic Form can be fully elucidated   The phenomenon of Steric Hindrance, which is dealt with at considerable length in Stewart's *Stereochemistry* (1907) affords an extensive field for study, but is deferred in order that the main features of the Theory may be submitted

It is well known that a large number of unsolved problems in Organic Chemistry await the result of further experiment and research   In view of this fact, it is submitted that the Theory of Atomic Form deserves the consideration of all who seek to unravel the mysteries of Atomic Affinity and Combination

The object which we had in view at the commencement of this book, was to design the form of the Carbon Atom, and by preparing aggregates of the carbonoid in various arrangements, to compare these with the carbon framework of a variety of carbon compounds   To a certain extent this has now been done, and features of interest have been presented   The Author regrets that so much in connection with the subject is necessarily deferred, but feels it to be his duty to lay before the public the results so far obtained

APPENDIX

It has been suggested to the Author that some information on the subject of model-making might be found helpful by those who desire to secure a more intimate knowledge of the carbonoid and its aggregates

It is certainly very desirable that those who wish to obtain a clear understanding of the Theory of Atomic Form should have samples of the models before them, as it has been found impossible by drawings and photographs to exhibit all the features of the carbonoid-aggregates or to shew all the combinations of which they are capable

Only one solid figure is required, viz, that of the carbonoid—of which a large number of plaster casts can be made from the same mould, all exactly alike All the figures of carbon chains, rings, &c, are prepared by gluing the carbonoids together to make the form of carbonoid-aggregate required

Materials The models may be cast in Plaster of Paris or Portland Cement or some other substance which will quickly set when poured into a mould The plaster casts are more easy to manipulate, but the cement models are stronger and more durable and less likely to be chipped or damaged In the case of the

plaster models, the solid edges and corners of the car-
bonoid are easily damaged, but the cement models are
harder and more difficult to rub down so as to produce
uniform and satisfactory faces to the figure   Plaster
of Paris (best quality) appears to be the best material
by reason of the promptitude with which it sets

The models made of Plaster of Paris may be
strenghtened by dipping them into a strong solution
of Size

Size   The size of the Carbonoid Model will depend
upon one measurement, A D or B C, Fig 9, p 13   The
length of this line decides the size of the entire figure
The Author has found a length of two inches a convenient
size   It would be easier to make accurate moulds to
a larger size, but the resulting casts would require more
material and in the case of rings of 60 carbonoids,
Fig 19, p 28b, would be unduly bulky   On the other
hand, if a smaller size be adopted, there is a difficulty
in securing sufficient accuracy in all the details of the
mould

The Mould   The preparation of an accurate mould
is of special importance and requires great care   It is
best to commence by preparing a gauge in the form of
Fig 9   It may be made out of ordinary sheet tin (or
more accurately tinned iron) and should be cut a trifle
larger than is desired and filed down to be strictly
accurate in all its proportions   From this gauge all
the measurements of the mould can be tested

The mould will have three sides, the fourth side of
the carbonoid being represented by the top of the mould,
which will be left open and the plaster smoothed to a

level surface   Each of these three sides may be pre-
pared by cutting a piece of sheet tin into the three
forms shewn below
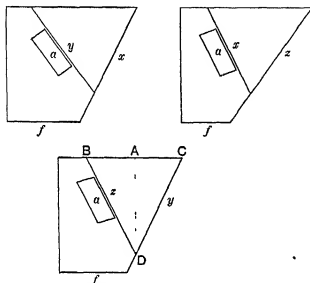
These drawings are made in a reduced size, but the pro
portions are accurate
    The guides are marked a
    Lines of contact are marked x x, y y and z z
    If the pieces when soldered together do not give a perfectly
horizontal surface for the 4th side of the carbonoid the feet f f f
may be adjusted to give the desired result

    The strips of tinned metal marked (a) should be
soldered in their places as guides before putting the
pieces together   A small space must be allowed for
the thickness of the tin, so that the interior of the mould
may be exact

J

The soldering together of the three sides of the mould is the most difficult operation, but is greatly assisted by having the guides in their right positions All the soldering must be on the *outside* so that the interior may be exact ; the difficulty is in getting the first pair of sides soldered together at the right angle to effect this an accurate model of the carbonoid in cardboard or wood should be prepared, and the mould can then be built up around the model

It is well to make a small pin hole at the bottom of the mould, in order to allow air to escape and prevent the models from being spoilt by bubbles at the bottom of the mould

We recommend the use of tinplate, medium to strong in thickness, so that the mould may preserve its proper contour

The importance of an accurate mould cannot be too strongly impressed upon the reader If all the faces of the carbonoid are not quite equal, or if the two solid angles at A C and B D, Fig 8, p 13, are not exactly 1/6th of four right angles there will be a difficulty in obtaining correct figures of the benzenoid, carbon chains, &c , and the preparation of the ring of 60 carbonoids will be a matter of considerable difficulty

Making   the   Models   The plaster should be thoroughly mixed and smooth, of the consistency of cream and be poured carefully into the mould, avoiding air bubbles It is best to mix a small quantity freshly for each model, and to fill the mould to overflowing As soon as the plaster begins to set, remove the surplus at the top of the mould with a knife and cut it down to a

surface level with the top of the mould After standing
until the plaster is quite set, invert the mould, and by
tapping it on the outside the cast will be loosened and
will fall out It should be handled carefully and set
aside until the next day, when it will be quite dry

A level surface at the top of the mould can be
secured by laying a smooth plate of metal on the top
and squeezing out all surplus plaster, but there is danger
of air bubbles forming under the plate and causing
irregularities in the surface

After making the cast, the mould should be cleaned
and the inside oiled, to prevent the plaster from
sticking to the mould when next used

When quite dry, the models may be rubbed down
on a sheet of medium to fine glass paper laid on a flat
board, to remove any irregularities, but care must be
taken not to reduce the size of the model by too much
rubbing

Making the Aggregates The carbonoids may be
affixed to one another by any strong material The
Author has used ordinary glue, but care must be
exercised not to apply too much If pressed tightly
together a small quantity of glue will make a good
joint, but the most useful material appears to be
" Necol " sold in tubes It is always ready for use,
dries quickly, makes a strong clean joint, and if care-
fully used will not run over or disfigure the aggregate ,
the latter may require rubbing down with glass paper,
and defects may be remedied by filling up holes, &c ,
with plaster

K

To write on the models ordinary ink should not
be used, but a small sable hair brush and Indian ink
or lead pencil

"Necol" may be used to strengthen the plaster
model and prevent damage to the edges and points, it
should be applied as a kind of paint to the outside
surface, smoothed down and allowed to dry

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